



Water Quality Research Program

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Assessing Chemical Constituents in Reservoir Tailwaters

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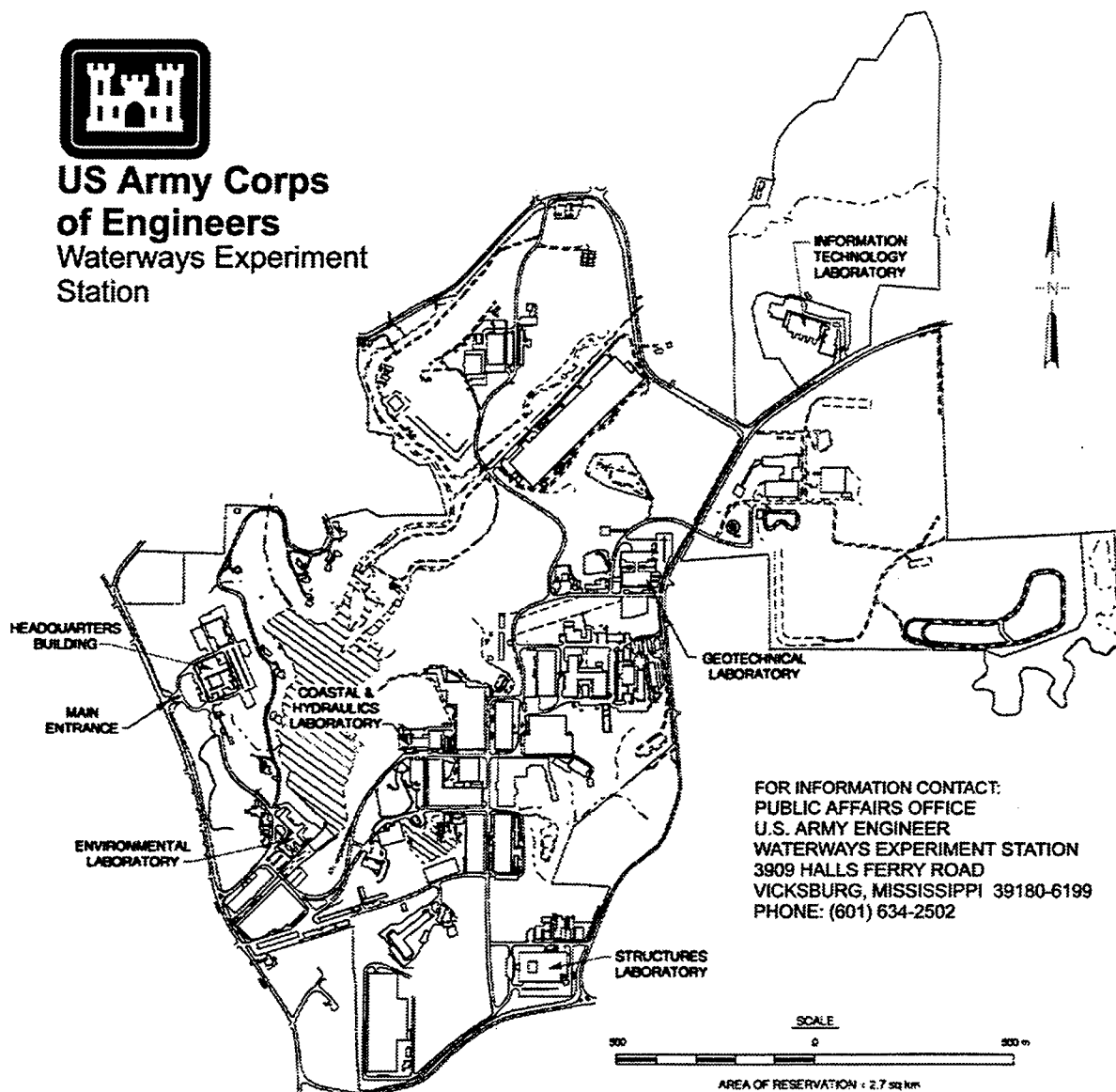
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Contents

Preface	v
1—Introduction and Objectives	1
2—Literature Review	4
Methods	4
Results and Discussion	4
3—Laboratory Studies	9
Methods	9
Results and Discussion	9
4—Field Studies	14
Methods	14
Results and Discussion	17
5—Conclusions and Recommendations	34
References	36
Appendix A: Annotated References and General References	A1
SF 298	

List of Figures

Figure 1.	Iron speciation with a,a'-dipyridyl in anoxic simulated tailwater following exposure to oxygen	10
Figure 2.	Iron speciation with ferrozine in anoxic simulated tailwater following exposure to oxygen	11
Figure 3.	Manganese speciation in anoxic simulated tailwater following exposure to oxygen	13
Figure 4.	Location of Nimrod Dam and Lake and tailwater sampling stations	15

Figure 5.	Water quality profiles in forebay of Nimrod Lake, 8/23/95	18
Figure 6.	Total carbon fractions at lower (a) and higher (b) releases	19
Figure 7.	Dissolved carbon fractions at lower (a) and higher (b) releases	20
Figure 8.	Alkalinity values at lower (a) and higher (b) releases	21
Figure 9.	Chloride, nitrate, and sulfate concentrations at lower (a) and higher (b) releases	22
Figure 10.	Temperature, pH, specific conductivity, and dissolved oxygen at Station A	23
Figure 11.	Temperature, pH, specific conductivity, and dissolved oxygen at Station B1	24
Figure 12.	Temperature, pH, specific conductivity, and dissolved oxygen at Station B3	25
Figure 13.	Iron speciation of reservoir release water at Lake Nimrod, Arkansas, August 1995	27
Figure 14.	Manganese speciation of reservoir release water at Lake Nimrod, Arkansas, August 1995	28
Figure 15.	Total and soluble iron at lower (a) and higher (b) releases	30
Figure 16.	Total and soluble manganese at lower (a) and higher (b) releases ...	31
Figure 17.	Results of photochemical reduction test of reservoir release water at Lake Nimrod, Arkansas	33

Preface

The work reported herein was conducted as part of the Water Quality Research Program (WQRP), Work Unit 32854. The WQRP is sponsored by the Headquarters, U.S. Army Corps of Engineers (HQUSACE), and is assigned to the U.S. Army Engineer Waterways Experiment Station (WES) under the purview of the Environmental Laboratory (EL). Funding was provided under Department of the Army Appropriation No. 96X3121, General Investigation. The WQRP is managed under the Environmental Modeling, Simulation, and Assessment Center (EMSAC), Dr. John W. Barko, Director for EL. Mr. Robert C. Gunkel was Assistant Director for the EMSAC. Program Monitor during this study was Mr. Frederick B. Juhle, HQUSACE.

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This report was prepared by Mr. Ashby and Ms. Amy S. Hall, EPEB; Drs. Stephen P. Faulkner and Robert P. Gambrell, Ms. Brenda A. Smith, and Mr. Paul E. Hintze, Louisiana State University, Baton Rouge, LA; and Dr. Joe Nix, Ouachita Baptist University, Arkadelphia, AR. Technical review was provided by Drs. Robert H. Kennedy and James M. Brannon, EPEB. Preparation of this report was under the general supervision of Dr. Richard E. Price, Chief, EPED, and Dr. John Harrison, Director, EL.

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1 Introduction and Objectives

The construction of a dam and reservoir to provide flood control, hydropower, recreation, navigation, and other purposes changes the river downstream of the dam. Typical changes to the river include alterations in the magnitude, duration, and timing of discharge, physicochemical changes associated with water quality processes in the upstream impoundment and the area downstream from the impoundment, and possible changes in the biotic community. The extent of these changes in the area downstream of the dam is a function of these alterations as well as downstream channel morphometry and substrate, hydrologic features such as inflows, and riparian conditions. The reach downstream of a dam is often referred to as the tailwater region, with downstream boundaries defined by confluences with secondary tributaries, downstream structures or impoundments, or a designated travel time as a function of discharge or physicochemical equilibrium.

Efforts to describe and quantify physicochemical changes in the tailwater region of reservoirs have been based on water quality processes described for aerobic processes in lakes and reservoirs using reaeration of anoxic hypolimnetic water (Chen, Gunnison, and Brannon 1983), changes in chemical constituents (Gordon, Bonner, and Milligan 1984; Nix 1986; Nix et al. 1991), and impacts of reservoir operations (Mathur, McClellan, and Haney 1988; Webb and Walling 1993; Barillier, Garnier, and Coste 1993; and Ashby, Kennedy, and Jabour 1995). Often studies of a particular constituent of interest provide processes information useful to other investigations. For example, while successful at predicting manganese oxidation under certain conditions, Hess, Kim, and Roberts (1989) attributed other environmental factors such as pH, precipitation, and unsteady flow with limiting application of an oxidation model for manganese in reservoir releases. Reduced rates of oxidation have also been attributed to the presence of complexing anions such as Cl^- and SO_4^{2-} (Sung and Morgan 1981) and complexation with organic carbon (Theis and Singer 1974; Knocke, Shomey, and Bellamy 1994). Prediction of physicochemical changes during steady-state releases has been conducted for many variables with the steady-state model, Tailwater Quality Model (TWQM) developed by Dortch, Tillman, and Bunch (1992). Dortch and Hamlin-Tillman (1995) were successful at predicting manganese concentrations in tailwaters of selected reservoirs during steady-state releases when consideration was given to substrate type. Although the mechanism of manganese removal was not investigated, both chemical (e.g., Stumm

and Morgan 1981) and biological (e.g., Nealson, Tebo, and Rosson 1988) mechanisms exist.

Chemical processes associated with iron oxidation have yet to be adequately described from field measurements for accurate prediction with the TWQM (Dortch, Tillman, and Bunch 1992). Additionally, Dortch, Tillman, and Bunch (1992) suggested inadequate speciation (the determination of the individual physicochemical forms of that element that together make up its total concentration in a sample (Florence 1982)) of iron via conventional field methods (i.e., filtration) limited prediction of oxidation of reduced iron in tailwaters. Size fractionation or use of chemical speciation based on pore size of a membrane filter may not be adequate to measure and then therefore describe species (Stumm and Morgan 1981). Effects of membrane filtration may also lead to incomparable results between sites (Horowitz, Elrick, and Colberg 1992). Interactions of biological, photochemical, homogeneous, and heterogeneous processes in iron oxidation kinetics described by Barry et al. (1994) demonstrate the complexity in assessing the processing of elements in aquatic systems. Even colorimetric methods for measuring reduced iron may be subject to interferences such as fulvic acid in oxic waters (Suzuki et al. 1992). Factors such as oxidation state, complexation with other elements, reactions with organic compounds, precipitation, adsorption, biological processes, and photochemical processes, all of which vary by element and local water quality, channel hydrology and morphology, and biotic community must be considered when speciation is required.

Florence (1982) provides a review of speciation of trace elements in water, listing possible physicochemical forms of metals in natural waters (Table 1) and a discussion of a variety of analytical techniques. The need for speciation of metals has been recognized in a number of investigations. Speciation of trace metals for

Table 1 Possible Physicochemical Forms of Metals in Natural Waters		
Physicochemical Form	Possible Examples	Approximate Diameter, nm
Particulate	Retained by 0.45- μ m filter	>450
Simple hydrated metal ions	$\text{Cd}(\text{H}_2\text{O})_6^{2+}$	0.8
Simple inorganic complexes	$\text{Pb}(\text{H}_2\text{O})_4\text{Cl}_2$	1
Simple organic complexes	Cu glycinate	1-2
Stable inorganic complexes	PbS , ZnCO_3	1-2
Stable organic complexes	Cu fulvate	2-4
Adsorbed on inorganic colloids	Cu^{2+} Fe_2O_3 , Pb^{2+} MnO_2	10-500
Adsorbed on organic colloids	Cu^{2+} humic acid	10-500
Adsorbed on mixed organic inorganic colloids	Cu^{2+} humic acid Fe_2O_3	10-500
Note: Florence 1982		

water quality criteria (Allen and Hansen 1996; Allen 1993a,b) and toxicity in aquatic systems (Benson et al. 1994) is necessary for a better understanding of bioavailability of trace metals to aquatic organisms. Toxicity is dependent on the physical and chemical forms of the metals (Luoma 1983; O'Donnell, Kaplan, and Allen 1985), and speciation rather than total concentration may improve understanding impacts on the biota (Kelly 1988). The water treatment industry has also recognized a need for speciation for determining appropriate application of oxidants for water treatment (Knocke, Shorney, and Bellamy 1994). Speciation of metals via analytical techniques may improve models with oxidation kinetics based on laboratory and field observations that used filtration for species differentiation.

Stumm and Morgan (1981) suggest that no single method presently available provides specific identification of a species, and they provide a general list of methods that may be used in combination to better describe the speciation of selected elements (Table 2). Often equilibrium models are used to decide the most likely complex form for a given metal ion within a water body of described conditions. However, since analytical methods exist for determining the oxidation state of selected elements, models that describe kinetics based on changes in oxidation states would benefit from improved measurements.

The objectives of this study were to (a) review current methods for analytical techniques for speciation of selected nutrients and metals with emphasis on measuring iron concentrations at different oxidation states (Fe^{2+} and Fe^{3+}), (b) evaluate applicable analytical techniques in laboratory studies, and (c) evaluate selected techniques in field investigations.

Table 2 Methods for Assisting in Specific Identification of Individual Species	
Method and Principle	Examples
<i>Physical-mechanical separation</i> Separation based on size (molecular weight), density, or charge	Membrane filtration, dialysis, electrodialysis, centrifugation, chromatography, gel filtration
<i>Auxiliary equilibria</i> A familiar equilibrium system (e.g., a color-forming reaction or an ion-exchange system) is introduced to provide indication for the species	Effect of complex formation on acid-base equilibrium, adsorption, ion-exchange or redox reaction, or solubility equilibrium; solvent extraction
<i>Equilibrium potentiometric methods</i> Evaluation of an electrical potential difference related to the chemical potential (activity) of certain species	Redox electrodes, ion-selective electrodes (metal, glass, hydrogen, solid-state, and membrane electrodes), electrodes of the second kind (e.g., Ag/AgCl)
<i>Electrode kinetics</i> Interdependence of current, potential, and time for a given electrode process; depends on the species participating	Polarography (square wave, pulse, inverse or anodic stripping), chronopotentiometry, chronoamperometry
<i>Direct detection of electrode or atomic structure</i> Measurement of properties based on electronic or atomic structure	Optical methods (spectrophotometry), magnetic properties (electron spin resonance), sound adsorption
<i>Catalytic effects and bioassays</i> Many species, especially metal ions, act as catalysts; growth (or inhibition) of organisms or rate of enzyme processes depends on species	Initiation of coordination of electron transfer reactions, batch or continuous-culture experiments with organisms, enzymatic reactions
Note: Stumm and Morgan 1981	

2 Literature Review

Methods

Analytical techniques with a high potential for field application were identified from a literature review conducted in 1993 of water resources abstracts, analytical abstracts, and chemical abstracts. The search logic was designed to limit the articles to analysis of water for each component with the search of chemical abstracts limited to the most recent years. Many of the 325 articles retrieved dealt primarily with an analytical methodology, but descriptive studies on distribution of elements in aquatic systems were also listed since these studies often include new or modified analytical methods.

Articles were then organized into four groups: (a) metals (iron and manganese, $n = 175$), (b) nitrogen (ammonia, nitrate, nitrite, $n = 84$), (c) sulfur (sulfate, sulfide, sulfite, $n = 50$), and (d) redox (oxidation reduction potential, $n = 16$). References with a high potential for field application were further reviewed with emphasis on field determination of oxidized and reduced forms of iron and manganese and are provided with annotation in Appendix A. Additional references (approximately 160) were reviewed, and appropriate references are included in Appendix A but not annotated. Detailed evaluations of nitrogen, sulfur, and redox techniques were not conducted as part of this study, and only limited analytical methods and references were included in Appendix A.

Results and Discussion

Initial review suggested that analysis of iron and manganese is dominated by atomic absorption (AA) techniques. There are variations that include direct aspiration, graphite furnace, and extractions prior to AA determination. Most of these methods probably produce results with operationally defined parameters such as dissolved iron with differentiation or speciation determined by pretreatment of the samples. In some cases, the extractions may be species specific. There were numerous references to electrochemical measurements such as voltammetry that are also often species specific and polarographic measurements that are specific for oxidation states (e.g., reduced iron and manganese, Davison 1977). Spectrophotometric methods (usually dependent upon color development) were often cited and

offer some opportunities for speciation. Application of electrochemical and colorimetric measurements (Wallman et al. 1993) describes advantages of polarographic techniques that simultaneously determine the concentration of both Fe^{2+} and Fe^{3+} in solution. Simultaneous spectrophotometric measurement of Fe^{2+} and Fe^{3+} has also been demonstrated at low levels in atmospheric water using di-2-pyridyl ketone benzoylhydrazone (DPKBH) as a colorimetric chelating agent (Pehkonen, Erel, and Hoffman 1992; Iha, Pehkonen, and Hoffman 1994). Ion chromatography was also referenced as a method to speciate metals. Commonly used analytical techniques for selected metals and nutrients (Table 3) are also provided in handbooks such as American Public Health Association (APHA) (1995) and U.S. Environmental Protection Agency (1979).

The use of colorimetric techniques for differentiating oxidized and reduced forms of iron and manganese were considered to have the highest potential for field application since these techniques often use portable equipment, commercially available reagents, and can provide rapid, onsite measurements. It should be noted that electrochemical techniques also offer a high potential for field application but may be limited by lack of familiarity of the techniques by field personnel.

Although there is no specific colorimetric method for measuring manganous (Mn^{2+}) manganese, Morgan and Stumm (1965) suggested that any manganese that passes through a 0.22- μm filter can be considered to be in the Mn^{2+} state when measured with formaldoxime. Formaldoxime has even been successfully used in colorimetric measurements of manganous concentrations in estuarine sediments (Armstrong, Lyons, and Gaudette 1979).

APHA (1995) provides a colorimetric method that uses 1-,10-phenanthroline to complex ferrous iron following reduction of all iron to the divalent oxidation state, Fe^{2+} . A variety of complexing agents have been used for determining ferrous iron concentrations. Bathophenanthrolinedisulphonic acid; 2',2'-dipyridyl (α, α' dipyridyl, see Müller (1932)); ferrozine (monosodium 3-(2-pyridyl)-5,6-bis(4-phenylsulphonic acid)-1,2,4-triazine, monohydrate, see Stookey (1970) and Gibbs (1976)); and TPTZ (2,4,6-tri(2'-pyridyl)-1,3,5-triazine) have been used in assessing iron fractions in filtered samples (Box 1984); however, changes in measured concentrations of ferrous complexes changed over time in the presence of a buffer, suggesting limitations for sample holding times. The use of bathophenanthroline (4,7-diphenyl-1,10 phenanthroline) for determination of Fe^{2+} in natural waters (Smith, McCurdy, and Diehl 1952) and in the presence of Fe^{3+} , ferric iron, has been characterized with inherent, small positive interferences under certain conditions (e.g., pH of analysis below 6.5 and Fe^{3+} is present, Macalady et al. 1982). The use of 2,2' bipyridyl for measurement of ferrous iron has been shown to be applicable (Heaney and Davison 1977), but sample handling is critical for accurate determinations. A thorough review of analytical methods for measuring oxidation states of iron in natural waters is provided in Pehkonen (1995).

Based on the literature review and with consideration to field applicability of available analytical techniques, colorimetric methods for determination of iron and manganese oxidation states were selected for further evaluation. Colorimetric

methods selected included the use of a,a',-dipyridyl and ferrozine for iron determinations and formaldoxime for manganese measurements.

Table 3
Analytical Methodologies From References Commonly Used in Environmental Analysis
Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983, U.S. Environmental Protection Agency, Cincinnati, OH
Iron
Method 236.1, Atomic Absorption, (direct aspiration)
Method 236.2, Graphite Furnace AA
Method 200.7, Inductively Coupled Plasma
Manganese
Method 243.1, Atomic Absorption, (direct aspiration)
Method 243.2, Graphite Furnace AA
Method 200.7, Inductively Coupled Plasma
Ammonia Nitrogen
Method 350.1 Colorimetric, Automated Phenate
Method 350.2 Titrimetric; Potentiometric, Distillation Procedure
Method 350.3 Potentiometric, Ion Selective Electrode
Nitrate
Method 352.1 Colorimetric, Brucine
Nitrite
Method 354.1 Spectrophotometric
Nitrate-Nitrite
Method 353.1 Colorimetric, Automated Hydrazine Reduction
Method 353.2 Colorimetric, Automated Cadmium Reduction
Method 353.3 Colorimetric, Manual Cadmium Reduction
Sulfate
Method 375.1 Colorimetric, Automated Chloranilate
Method 375.2 Colorimetric, Automated Methylthymol Blue, AA II
Method 375.2 Gravimetric
Method 375.4 Turbidimetric
(Sheet 1 of 3)

Table 3 (Continued)
Sulfide
Method 376.1 Titrimetric, Iodine
Method 376.2 Colorimetric, Methylene Blue
Sulfite
Method 377.1 Titrimetric
<i>Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, American Public Health Association, Washington, DC</i>
Iron
Method 315 A, Atomic Absorption Spectrophotometric
Method 315 B, Colorimetric, Phenanthroline
Manganese
Method 319 A, Atomic Absorption Spectrophotometric
Method 319 B, Colorimetric, Persulfate
Ammonia
Method 417 A, Preliminary Distillation Step
Method 417 B, Colorimetric, Nesslerization
Method 417 C, Colorimetric, Phenate
Method 417 D, Titrimetric
Method 417 E, Ammonia Selective Electrode
Method 417 F, Automated Phenate
Nitrate
Method 418 A, Ultraviolet Spectrophotometric Screening
Method 418 B, Nitrate Electrode Screening
Method 418 C, Cadmium Reduction
Method 418 D, Chromotropic Acid
Method 418 E, Devarda's Alloy reduction
Method 418 F, Automated Cadmium Reduction
Nitrite
Method 419, Azo Dye Production
(Sheet 2 of 3)

Table 3 (Concluded)
Sulfate
Method 426 A, Gravimetric
Method 426 B, Gravimetric
Method 426 C, Turbidimetric
Method 426 D, Automated Methylthymol Blue
Sulfide
Method 427 A, Separation of Soluble and Insoluble Sulfide
Method 427 B, Sample Pretreatment to Remove Interfering Substances or to Concentrate Sulfide
Method 427 C, Methylene Blue
Method 427 D, Iodometric
Sulfite
Method 428, Titrimetric
(Sheet 3 of 3)

3 Laboratory Studies

Methods

Selected colorimetric techniques for iron and manganese determinations were evaluated in laboratory studies prior to application in field studies. Comparisons of colorimetric methods for measuring concentrations of iron at specific oxidation states that use a,a',-dipyridyl and ferrozine were conducted to evaluate each method and differentiation via filtration. Tests were conducted on simulated reservoir water of known concentrations of iron and manganese. The simulated reservoir water was treated with nitrogen to remove dissolved oxygen and then aerated, thus simulated reaeration of anoxic hypolimnetic releases and the associated speciation of iron and manganese. Specific methods for determining reduced forms of iron and manganese and total concentrations were used; concentrations of oxidized forms were calculated by subtraction of reduced forms from the total concentration. Total iron in each sample was determined following the addition of 1.0 ml 10 percent $\text{NH}_2\text{OH}\cdot\text{HCl}$ prior to adding the ferrozine. This reduces the Fe^{3+} to Fe^{2+} prior to complexation with the colorimetric reagent. Manganese was analyzed using formaldoxime colorimetric reagent that quantifies the Mn^{2+} form of Mn on samples passing through a 0.22- μm filter (Morgan and Stumm 1965). Colorimetric determinations were conducted on unfiltered and filtered (0.4-, 0.2-, and 0.1- μm filters) samples immediately before aeration began (0 hr) and at 6, 26, and 50 hr after aeration at 520 nm (a,a',-dipyridyl) or 526 nm (ferrozine) for iron and at 450 nm (formaldoxime) for manganese on both a Perkin Elmer Lambda 3 and a Milton Roy Mini 20 spectrophotometer.

Results and Discussion

Both ferrozine and a,a',-dipyridyl are reliable colorimetric indicators of ferrous iron. Ferrozine was considered to be more applicable for determination of ferrous iron based on study results (Figures 1 and 2) particularly when results are read as percent transmission on the portable Milton Roy Mini 20 spectrophotometer. Filtration to differentiate oxidized and reduced iron was considered to be independent of filter pore size. There was some loss in total iron from the solution over the duration of the study that was unexplained but may be the result of precipitation of particulate iron, adhesion to the glass container, or incomplete digestion of total iron

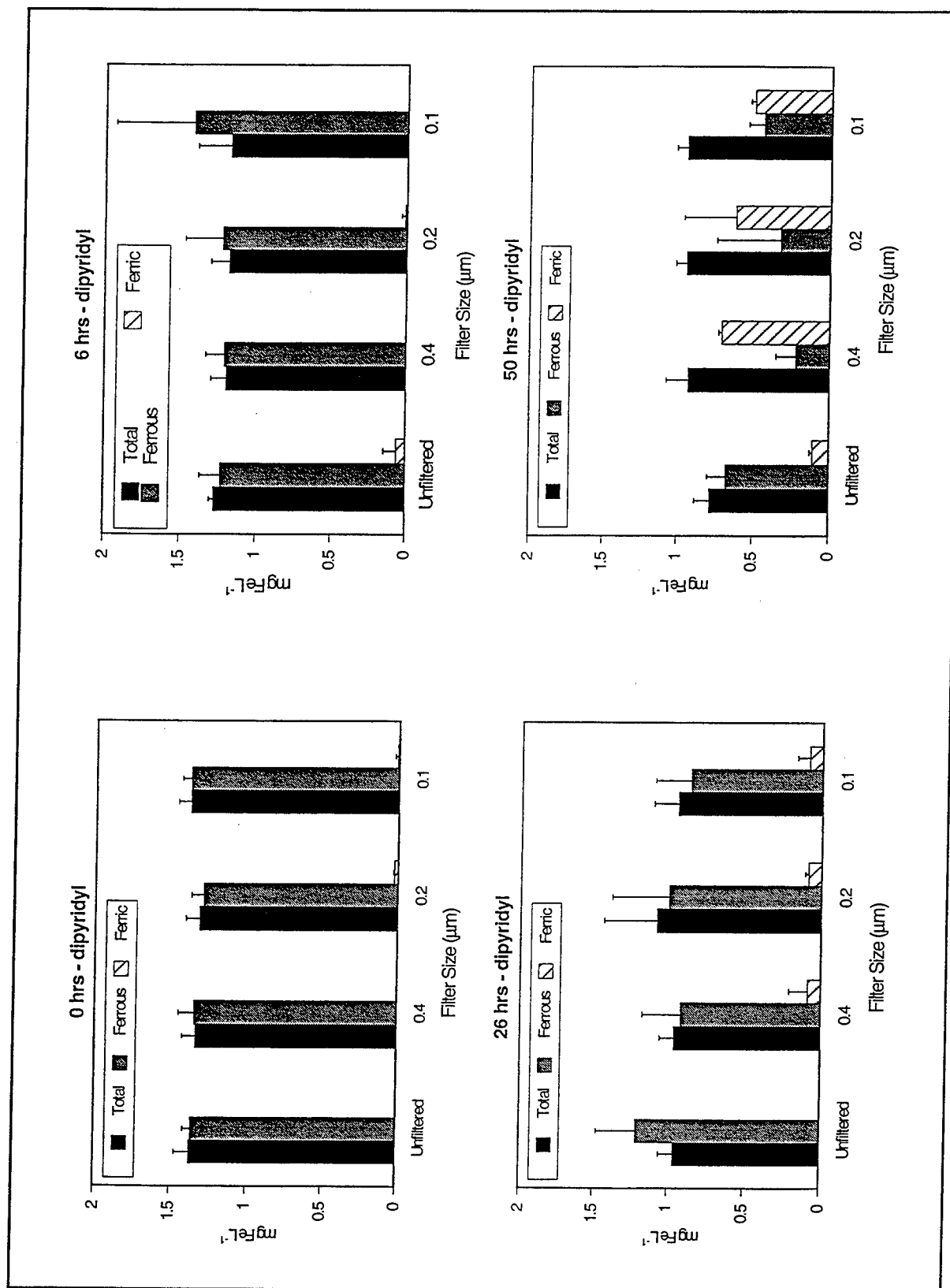


Figure 1. Iron speciation with a,a'-dipyritydi in anoxic simulated tailwater following exposure to oxygen

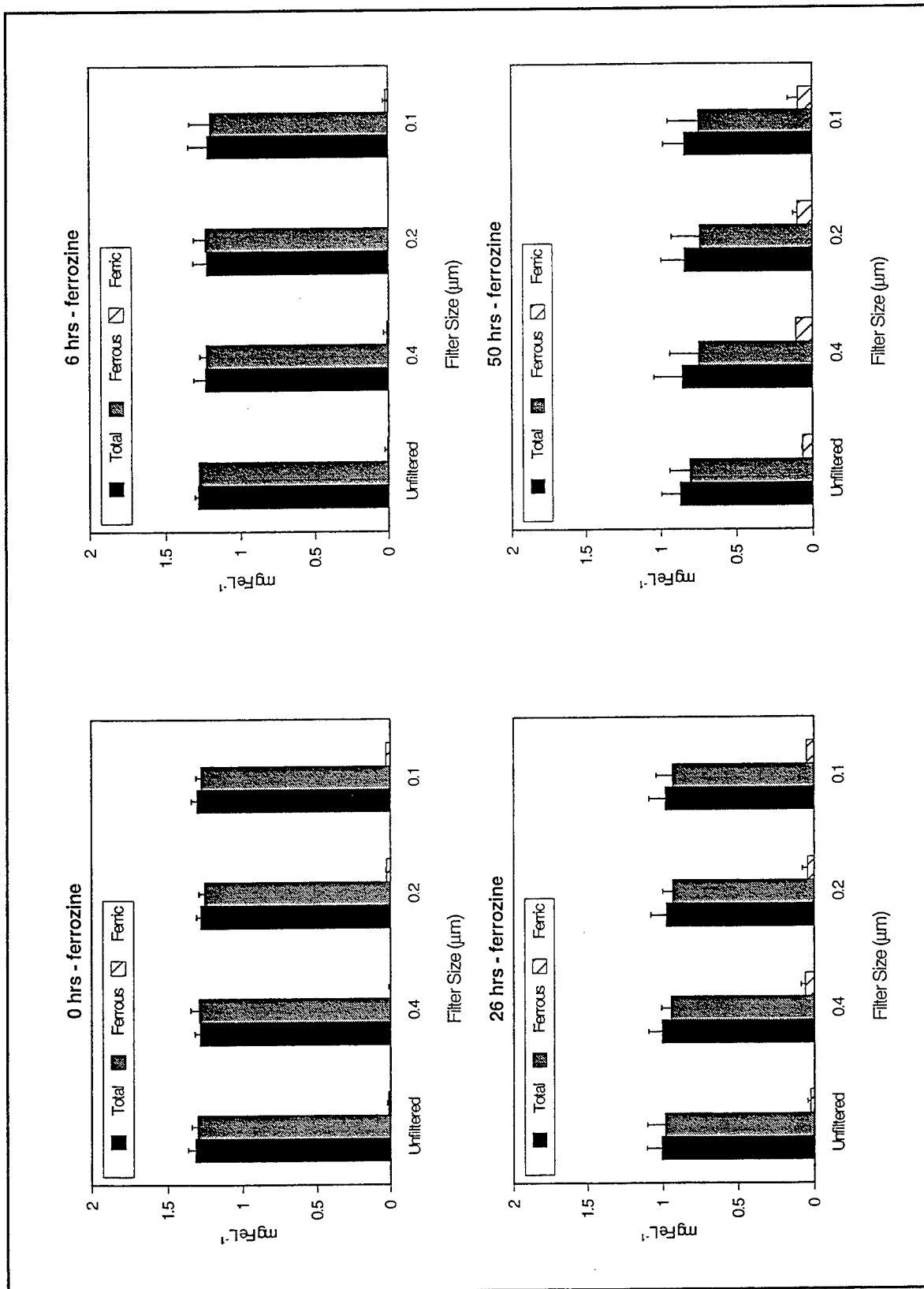


Figure 2. Iron speciation with ferrozine in anoxic simulated tailwater following exposure to oxygen

after aeration. Analytical anomalies indicate that best results are obtained when samples are analyzed as soon as possible with minimal sample handling. Furthermore, these studies were conducted on synthetic reservoir water with controlled chemical concentrations and would not account for interferences such as those previously described or other sources of error.

Determination of the oxidation state of manganese via filtration (i.e., Mn^{2+} only passing through a filter) was considered acceptable, and only filter pore sizes were evaluated. Manganese in the simulated reservoir water was primarily in the reduced, manganous (Mn^{2+}) form and remained in that form throughout the study (Figure 3). Observations of oxidized manganese at Hour 6 were considered to be a sampling artifact. Measurements were similar for each filter pore size, which would be expected in the absence of oxidation and subsequent particulate formation, precluding any evaluation of differentiation via filtration. Results of these laboratory studies have been more thoroughly described in Faulkner, Gambrell, and Ashby (1996).

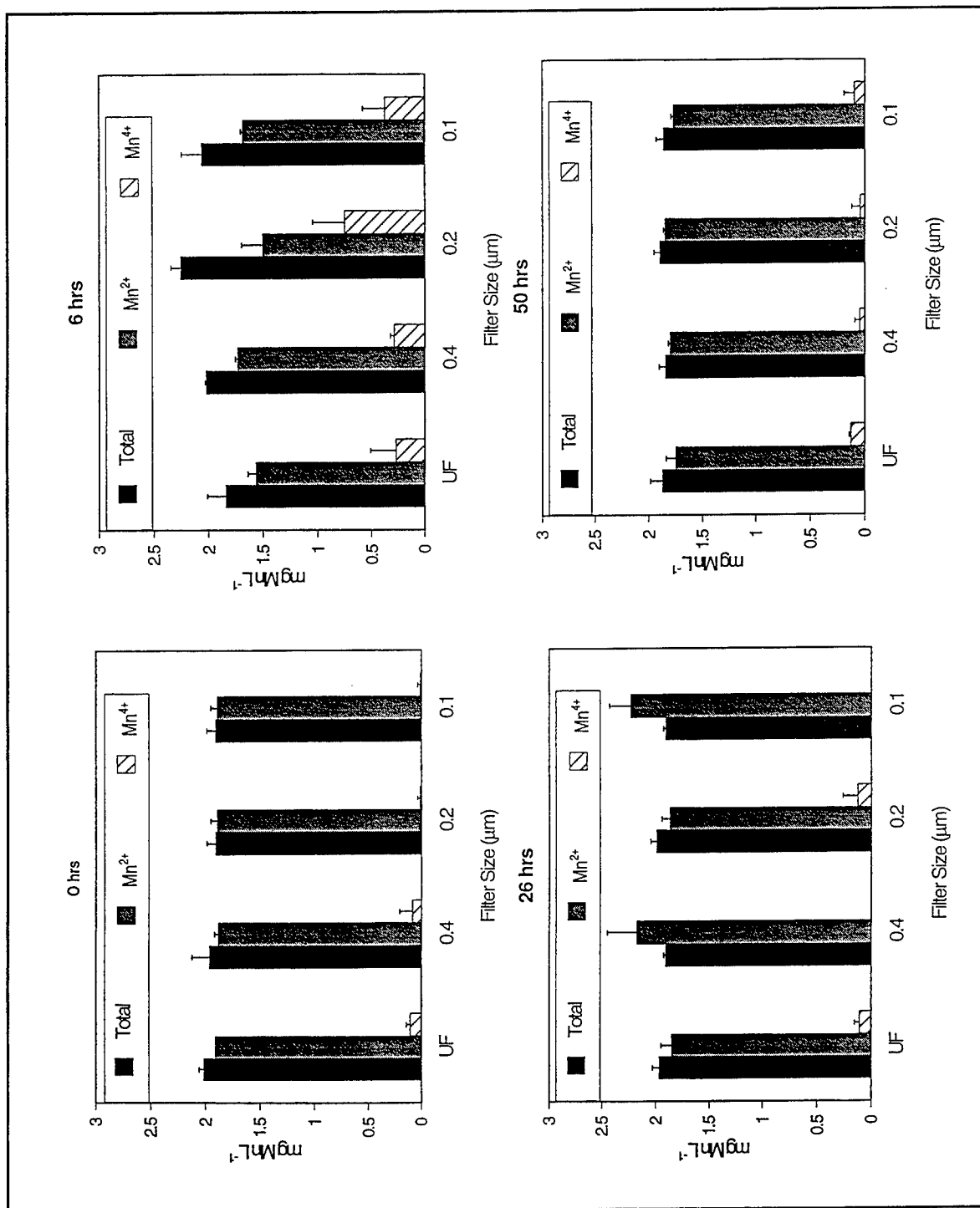


Figure 3. Manganese speciation in anoxic simulated tailwater following exposure to oxygen

4 Field Studies

Methods

Field studies were conducted at Nimrod Lake, Arkansas, to evaluate analytical methods developed in laboratory studies and describe water quality processes in the release. Nimrod Lake is a reservoir on the Fourche La Fave River in west-central Arkansas (Figure 4), 101 km upstream from its confluence with the Arkansas River. The rugged and wooded drainage area is about 1,760 km² or about 61 percent of the Fourche La Fave basin. Nimrod Lake is formed by Nimrod Dam, which is operated primarily for flood control and typically has a minimal release during stratification to provide for low flow in the Fourche La Fave River. The low-flow release is from the hypolimnion via Howell-Bunger valves (the center line of the penstock is approximately 7.6 m above the streambed elevation). The valves provide a discharge above the elevation of the tailwater that falls into a stilling basin. This type of discharge provides considerable aeration of the hypolimnetic release, which impacts dissolved oxygen concentrations and iron and manganese dynamics.

Nimrod Lake was selected based on the availability of information about channel morphometry, substrate type, travel time of steady-state releases, and dynamic iron and manganese processes in the release. Sampling design was similar to previous studies conducted by Nix et al. (1991) for comparative purposes. Sampling was conducted at Stations A, B1, and B3 to describe conditions in the immediate tailwater (A-B1) and at a downstream location (Figure 4). These stations were selected since previous studies indicated that iron and manganese processing was most obvious in the pool between A and B1 and conditions downstream were not what was anticipated for iron.

Initial conditions of low flow (near 0.6 m³ sec⁻¹ or 20 ft³ sec⁻¹) were sampled prior to an increase in release to near 2.8 m³ sec⁻¹ or 100 ft³ sec⁻¹ (referred to as high flow), which was held near constant for the remainder of the study to allow the reestablishment of steady-state conditions. The increase in flow was initiated at 1500 on August 22, 1995, and held until 1700 on August 23, 1995. The increased discharge was about half the discharge of previous studies to provide an additional data set for model evaluation under different flow conditions.

Sampling was conducted at each station during the increased release based on estimated travel time to describe water quality conditions of a parcel of release

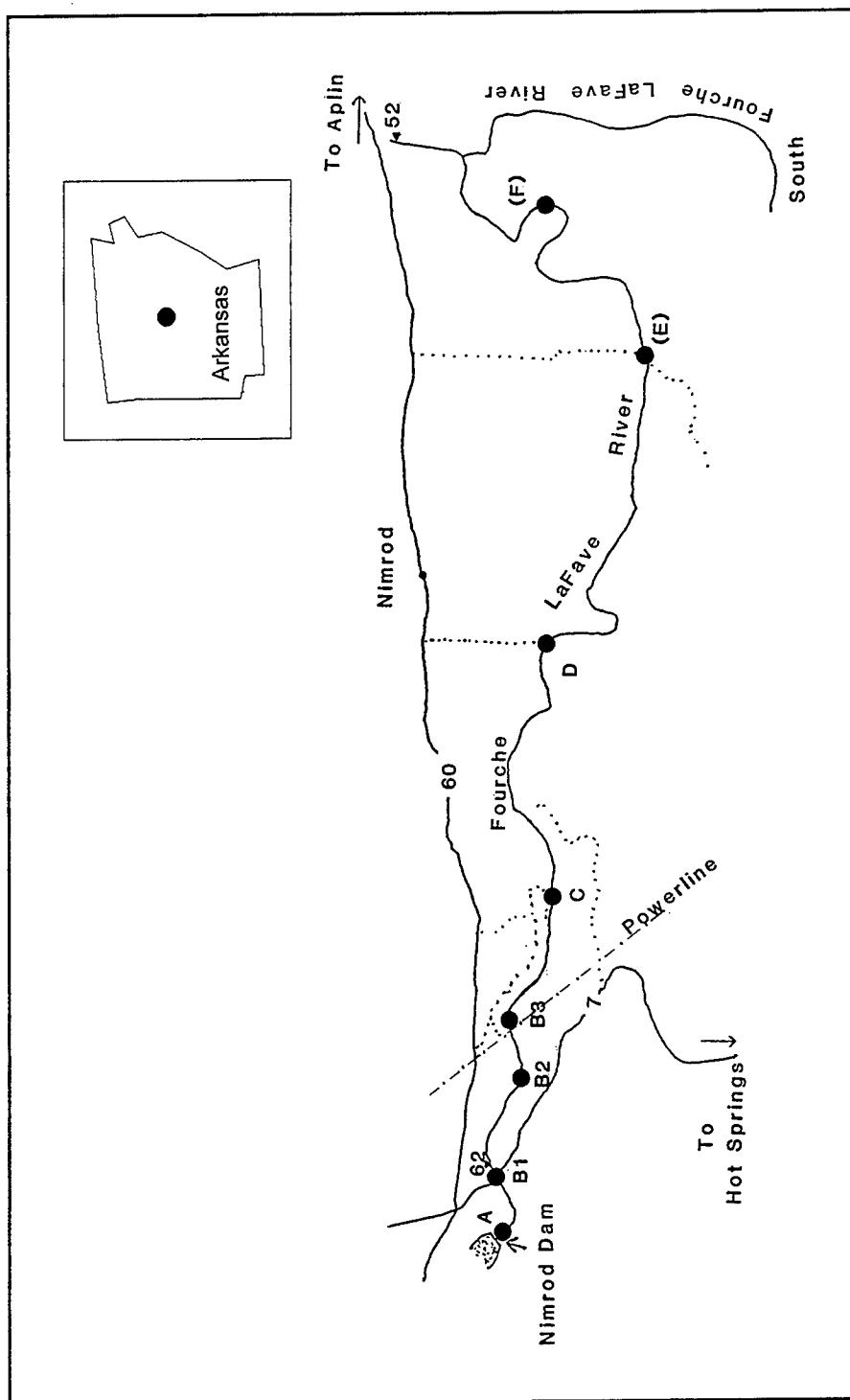


Figure 4. Location of Nimrod Dam and Lake and tailwater sampling stations

water over time during steady-state conditions. Time of travel was determined based on estimates from the TWQM, previous measurements using fluorescent dyes, and physical observations of neutrally buoyant floats. Temperature, dissolved oxygen, pH, and specific conductivity were monitored with Hydrolab data sondes at each site during the period of increased release to describe temporal changes. An in-lake profile of temperature, dissolved oxygen, pH, specific conductivity, and oxidation-reduction potential was conducted in the forebay region of the lake during the study to describe vertical gradients. One water sample was collected with a Van Dorn sampler from near the lake bottom for analysis of oxidized and reduced iron and manganese in the hypolimnion.

Water quality samples for iron and manganese analyses were collected at each location in the tailwater during the low-flow and high-flow releases as grab samples. Three 1-l samples were collected; one aliquot was analyzed without filtration, while the remaining sample was vacuum filtered through a 0.45- μm filter to remove the mass of particulate matter, then filtered through 0.4-, 0.2-, and 0.1- μm filters with in-line syringe holders. Ferrous iron was determined in both filtered and unfiltered samples with ferrozine. Five milliliters of each sample was added to 1.0 ml of ferrozine reagent. This was diluted to 10 ml total volume with distilled, deionized water and read at 565 nm on a Milton Roy Mini 20 spectrometer. Total iron in each sample was determined by the same procedure with the addition of 1.0 ml 10 percent $\text{NH}_2\text{OH}\cdot\text{HCl}$ prior to adding the ferrozine.

Manganous manganese was determined in both the filtered and unfiltered samples with formaldoxime. Five milliliters of each sample was adjusted to a basic pH with 1.5 ml of 5 M NaOH prior to the addition of 0.5 ml of formaldoxime reagent. This was diluted to 10 ml total volume with distilled, deionized water and read at 450 nm on a Milton Roy Mini 20 spectrometer. Total manganese in each sample was determined by the same procedure with the addition of 1.0 ml 10 percent $\text{NH}_2\text{OH}\cdot\text{HCl}$ prior to adding the formaldoxime. This reduces the Mn^{4+} to Mn^{2+} prior to complexation with the colorimetric reagent.

Two replicate samples were collected in 20-ml scintillation vials at each station, including the reservoir near-bottom sample, for analysis of total and soluble iron and manganese. Soluble metal samples were filtered with 0.45- μm filters in the field and preserved with three drops of nitric acid to reduce the pH to at least 2. The samples were transferred to the Wetland Biogeochemistry Institute (WBI) at Louisiana State University for iron and manganese analysis using a Jarrell-Ash Atom Comp Series 800 ICP. The detection limits on this instrument for iron and manganese are 0.025 and 0.02 ppm, respectively. Total and dissolved carbon samples were collected in 50-ml polyethylene bottles, filtered with 0.45- μm filters, and preserved with two drops of sulfuric acid to a pH of at least 2. Samples were transferred to the WBI for total and dissolved organic carbon determinations using an Ionics Model 1270 H analyzer with a detection limit of 1 ppm. Chloride, nitrate, and sulfate samples were collected in 20-ml scintillation vials and kept on ice for sample preservation. Samples were transferred to the WBI for analysis on the Dionex Model 2010i Ion Chromatography System with a detection limit of 0.01 ppm. Alkalinity and sulfide samples were collected in 500-ml amber bottles and transferred to an onsite laboratory for analysis. Alkalinity was measured via

titration (American Public Health Association 1995). Sulfide analysis consisted of extracting 5 ml of the water sample and transferring it to a 20-ml scintillation vial that contained 5 ml of an antioxidant buffer, which prevents the oxidation of sulfide. Sulfide concentrations were then determined with the LAZAR Model IS-146 Sulfide Electrode with a detection limit of 0.01 ppm.

Six 1- ℓ water samples were collected in clear glass bottles at Station A for determining the importance of photochemical oxidation at this site. Three samples were wrapped in aluminum foil to prevent light penetration, and three were left unwrapped. All six samples were then incubated from 1000 to 1700 hr in the open sunlight at ambient temperatures. Samples were collected at several intervals during the incubation period for ferrous iron analysis.

Results and Discussion

Initial conditions were determined by in-lake water quality which may be inferred from sampling in the forebay. Profiles of temperature indicate a stratified system with temperatures ranging from 31.3 °C in the surface to 24.7 °C in the bottom (Figure 5a), resulting in an anoxic hypolimnion (Figure 5b). Specific conductivity displayed maximum concentrations near the bottom and relative oxidation-reduction values (the instrument was not calibrated for oxidation-reduction) decreased in the hypolimnion coincident with anoxia (Figures 5c and 5d). Values of pH ranged from 9.0 in the surface to 8.0 in the bottom.

The effects of changing flow, which changes residence time in the channel, were apparent for most constituents measured at 0.6 and 2.8 m³ sec⁻¹, with concentrations decreasing with distance at the lower flow and remaining relatively constant at the higher flow (Figures 6 through 9). During low flow, total carbon decreased from near 12.5 mg ℓ^{-1} at Station A to near 9.3 mg ℓ^{-1} at Station B3, with the trend of decreasing concentrations continuing downstream (Station D). At the constant flow of 2.8 m³ sec⁻¹, total carbon concentrations remained near 12 mg ℓ^{-1} , and inorganic and organic fractions concentrations varied little with distance. Decreased total carbon concentrations at the lower flow were attributed to the loss of inorganic carbon, as indicated by the decrease in total inorganic carbon concentration with distance and relatively constant total organic carbon concentrations (Figure 6a and 6b). Patterns for dissolved carbon fractions were similar to those of total carbon fractions (Figure 7a and 7b). Dissolved fractions accounted for about 83 percent of the total carbon fraction, with dissolved organic carbon accounting for over half of the total carbon and three-fourths of the total organic carbon. Alkalinity concentrations decreased from near 29 mg ℓ^{-1} CaCO₃ to near 20 mg ℓ^{-1} CaCO₃ at Station B3 during low flow, yet remained constant near 25 mg ℓ^{-1} CaCO₃ during the steady-state release of 2.8 m³ sec⁻¹ (Figure 8a and 8b). With the exception of nitrate concentrations at the 0.6-m³ sec⁻¹ release, chloride, nitrate, and sulfate concentrations were relatively constant at both release levels and at similar values (Figure 9a and 9b). Nitrate concentrations during the 0.6-m³ sec⁻¹ release increased with distance from near 0.3 mg ℓ^{-1} at Station A to 1.4 mg ℓ^{-1} at Station B3 before decreasing to near

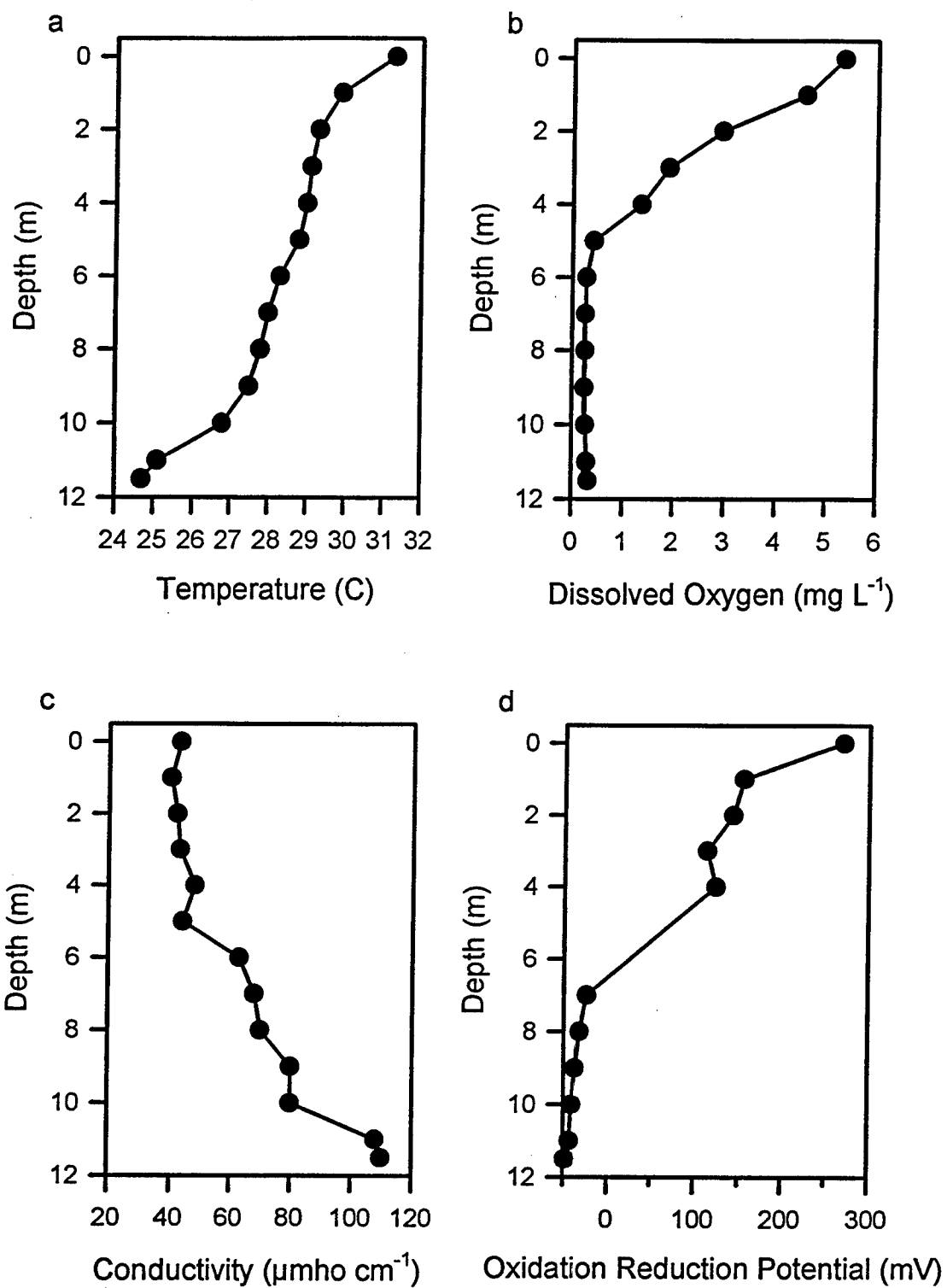


Figure 5. Water quality profiles in forebay of Nimrod Lake, 8/23/95

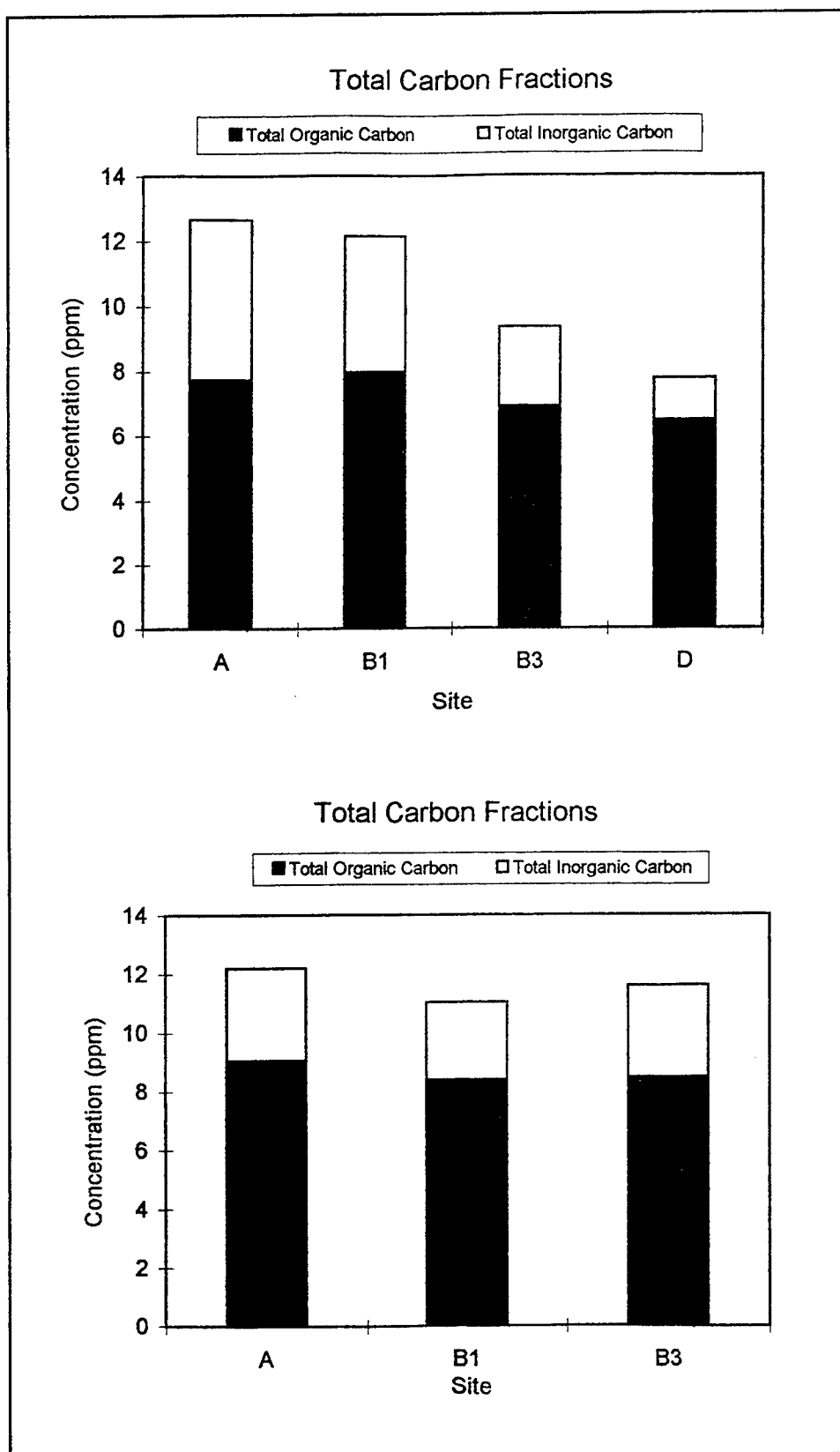


Figure 6. Total carbon fractions at lower (a) and higher (b) releases

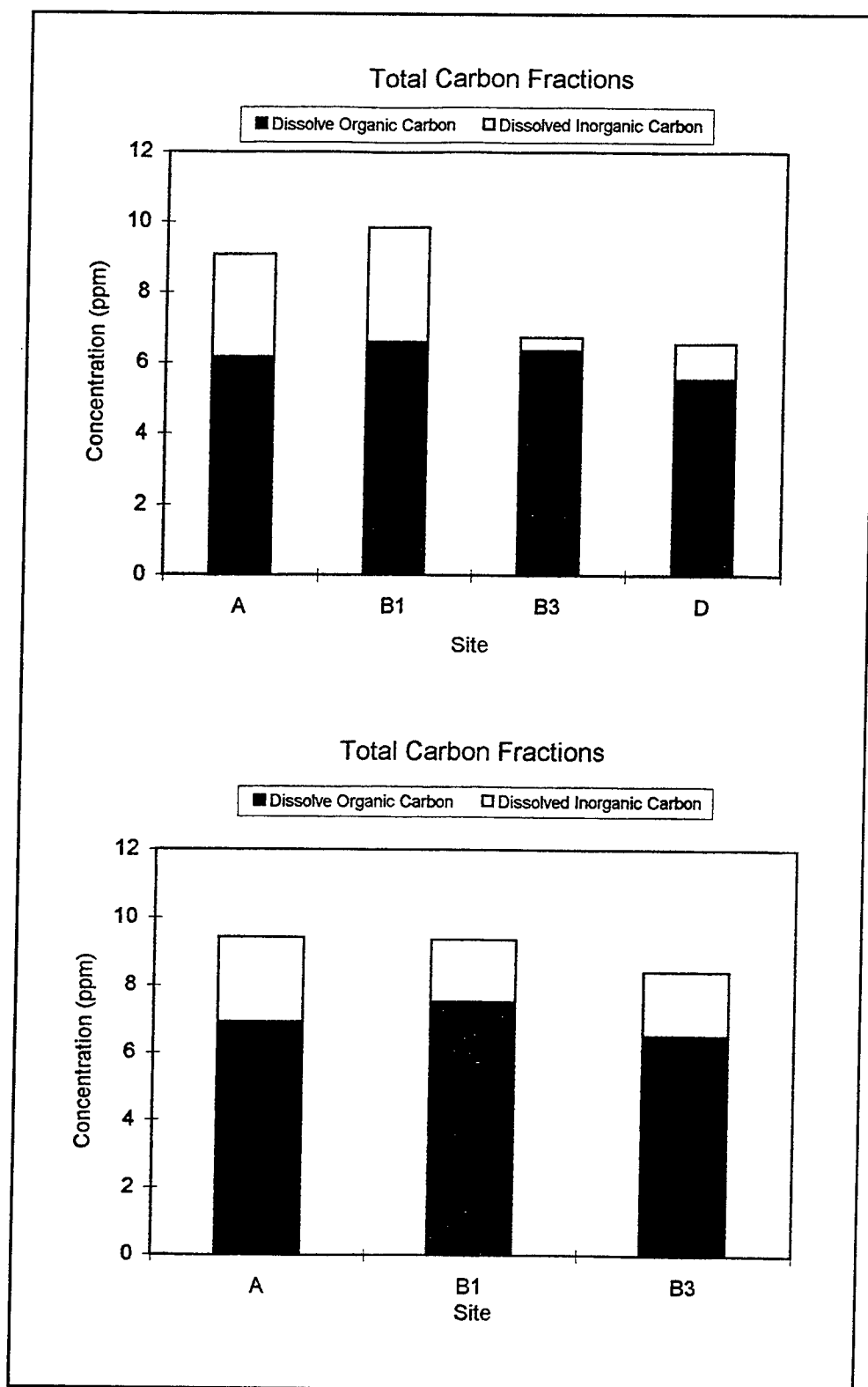


Figure 7. Dissolved carbon fractions at lower (a) and higher (b) releases

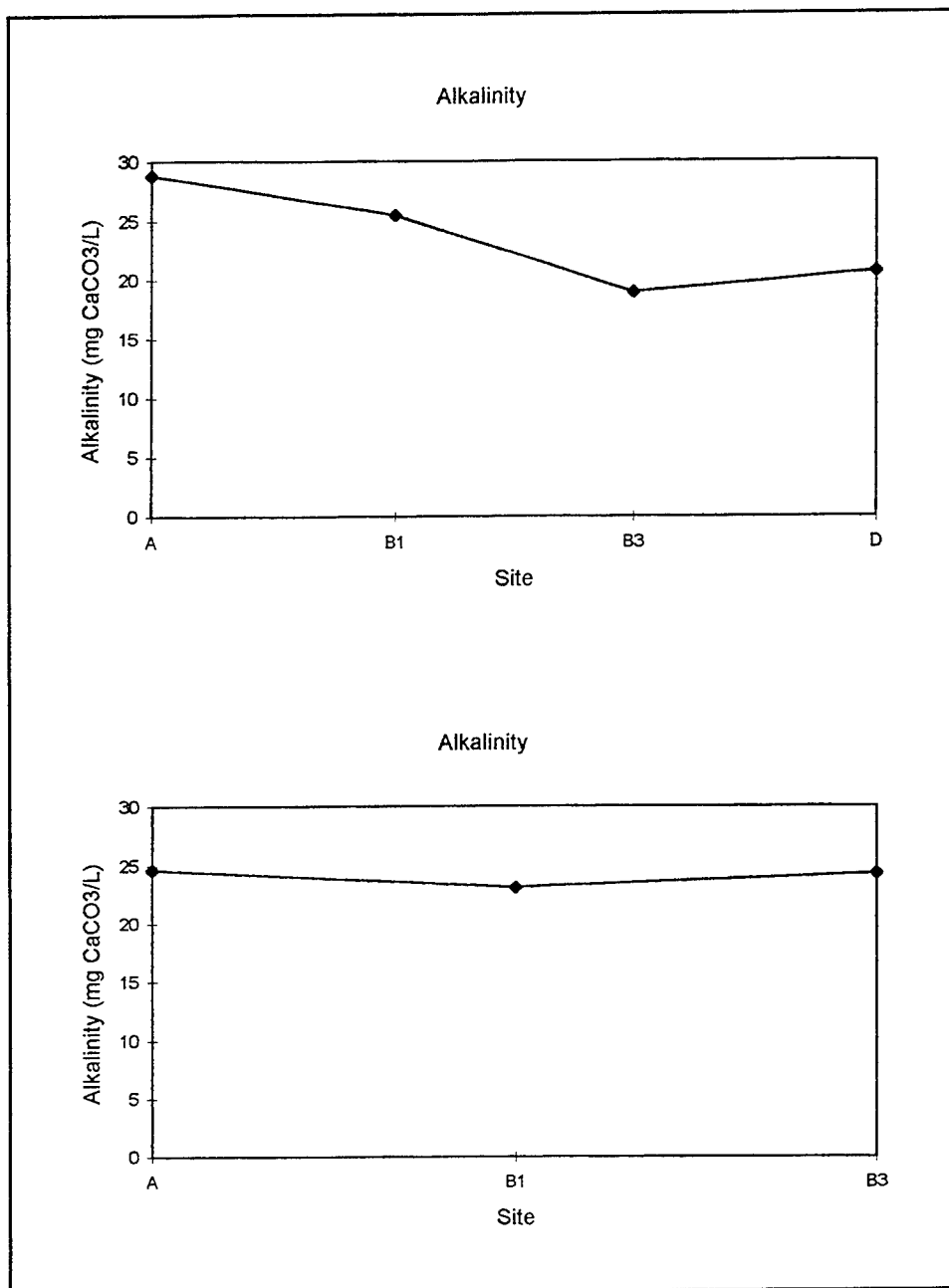


Figure 8. Alkalinity values at lower (a) and higher (b) releases

0.7 mg ℓ^{-1} further downstream. Sulfide levels were below the detection limit for the majority of the sites.

Steady-state conditions were described for the sustained release of 2.8 m³ sec⁻¹ with continuous monitoring of temperature, dissolved oxygen, pH, and specific conductivity at Stations A, B1, and B3 (Figures 10 through 12). Conditions at Station A remained relatively constant with the exception of dissolved oxygen concentrations, which tended to decrease with time. Field verification of dissolved

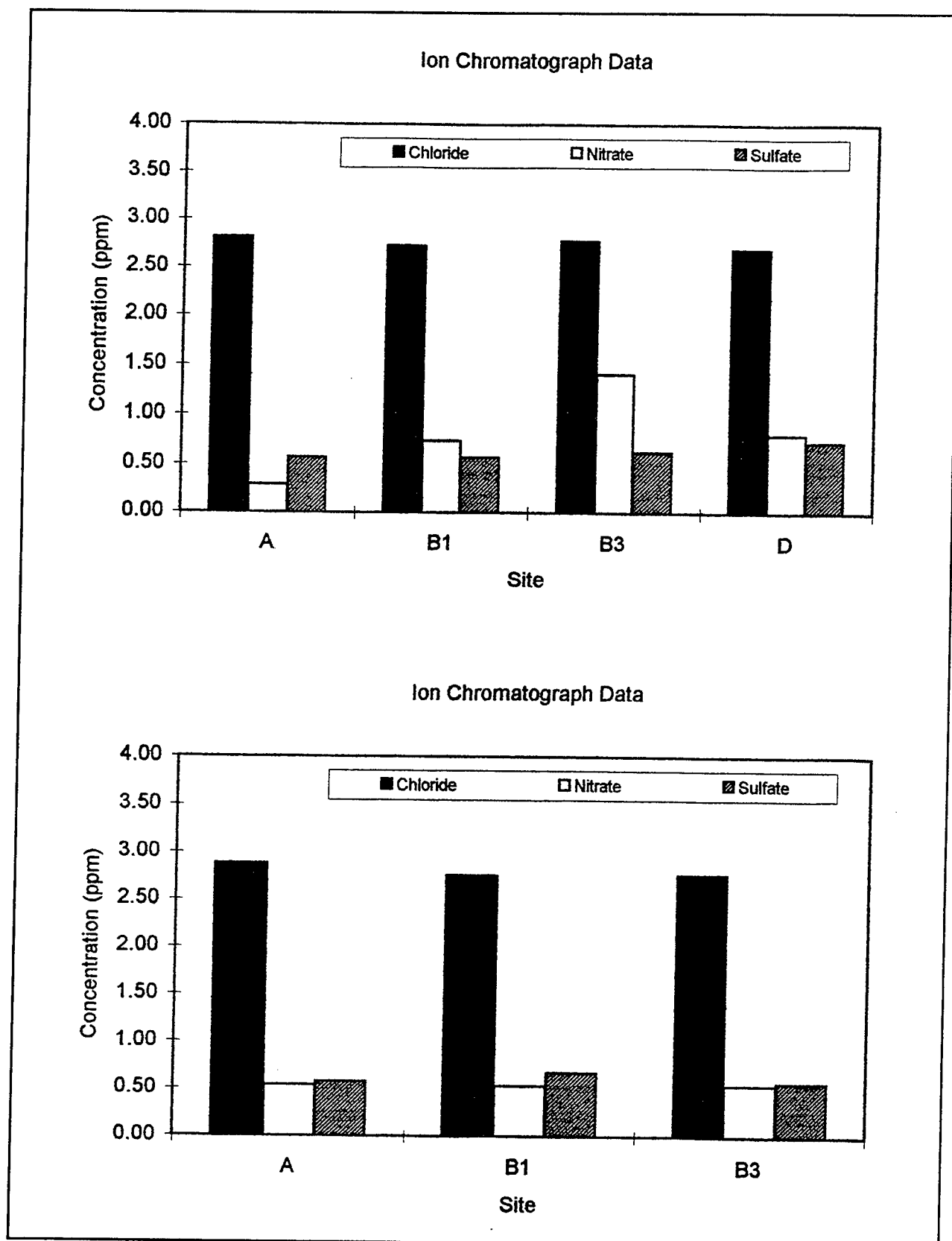


Figure 9. Chloride, nitrate, and sulfate concentrations at lower (a) and higher (b) releases

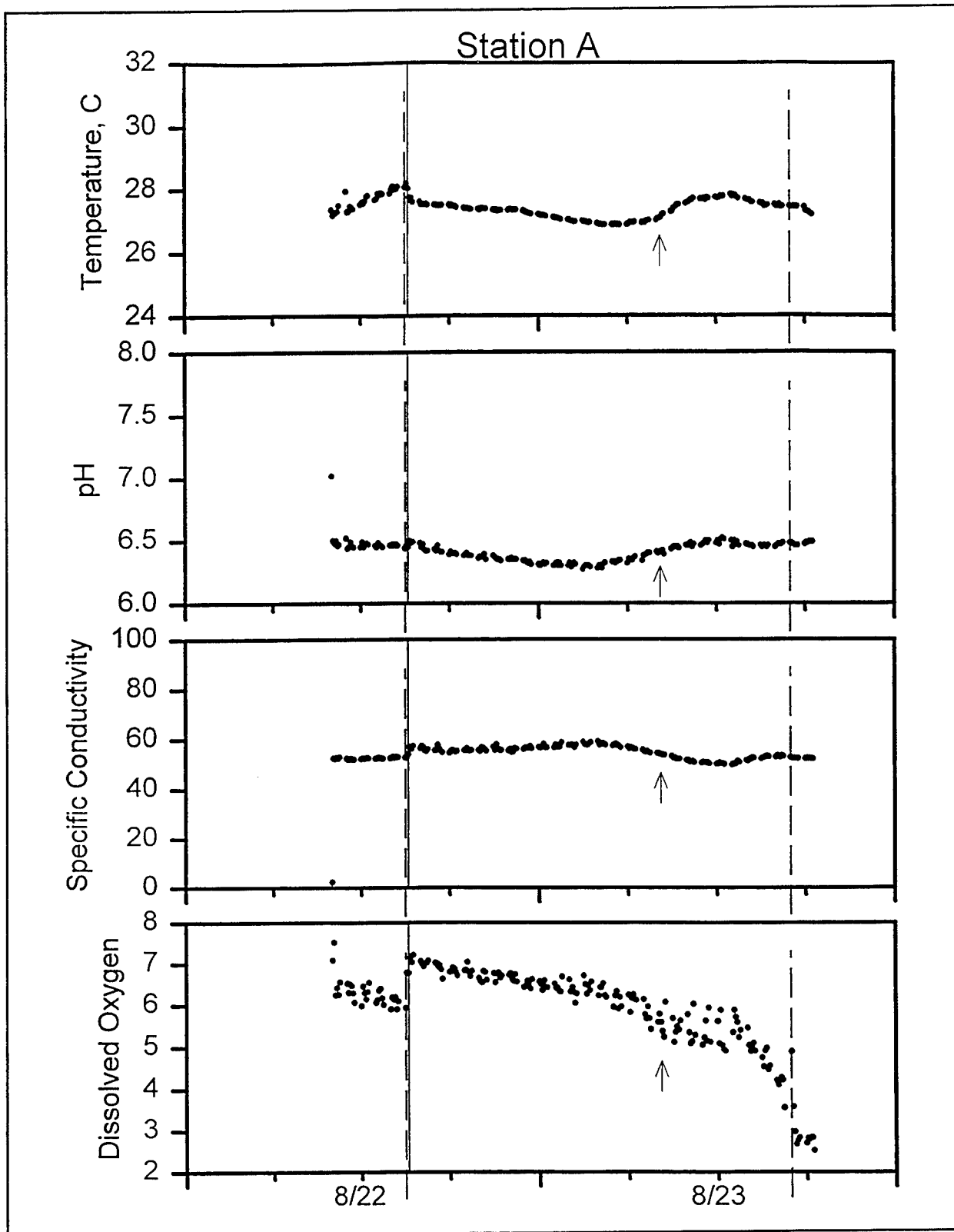


Figure 10. Temperature, pH, specific conductivity, and dissolved oxygen at Station A (Dashed line denotes steady-state discharge. Solid line denotes estimated travel time. Arrow denotes sampling time)

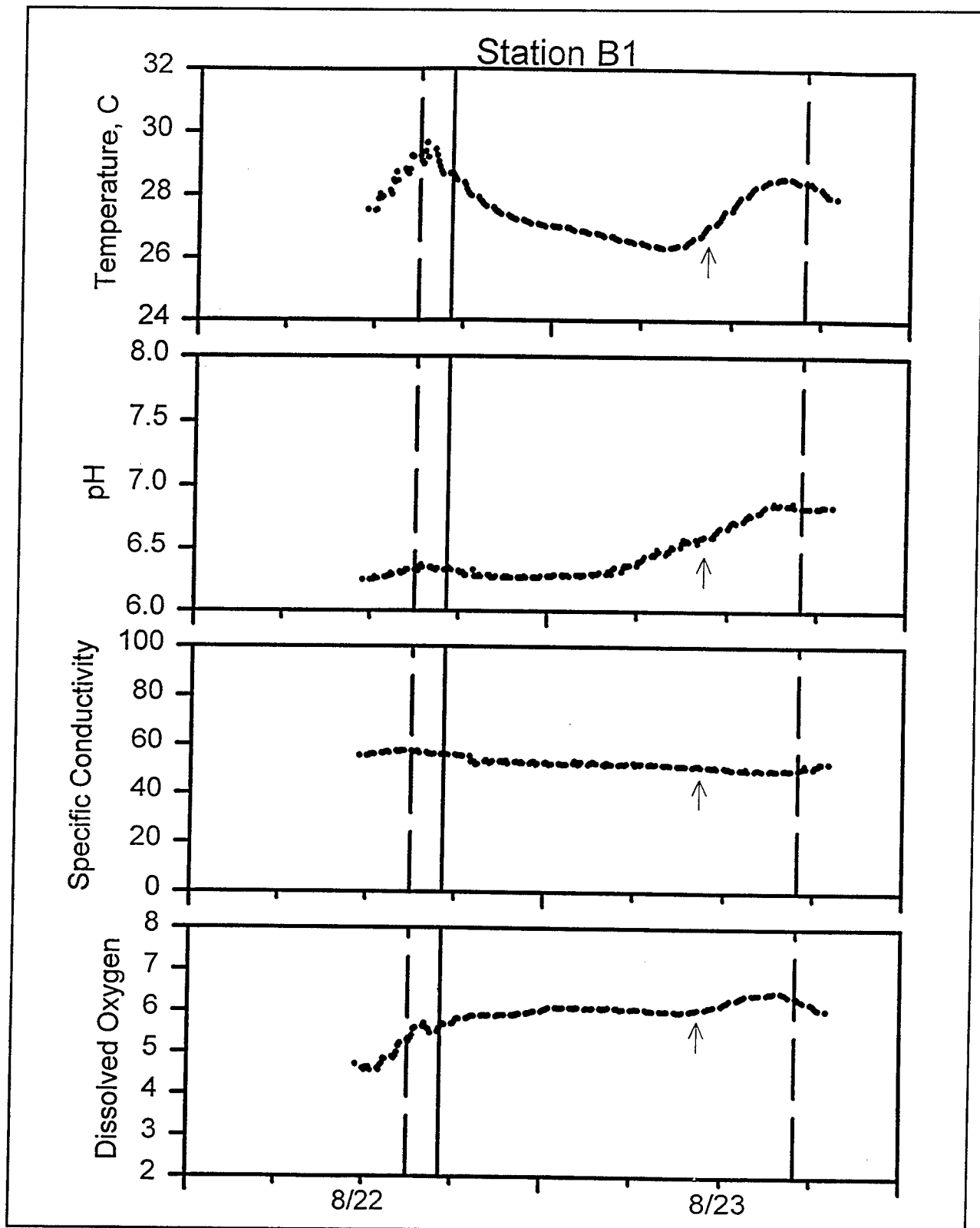


Figure 11. Temperature, pH, specific conductivity, and dissolved oxygen at Station B1 (Dashed line denotes steady-state discharge. Solid line denotes estimated travel time. Arrow denotes sampling line)

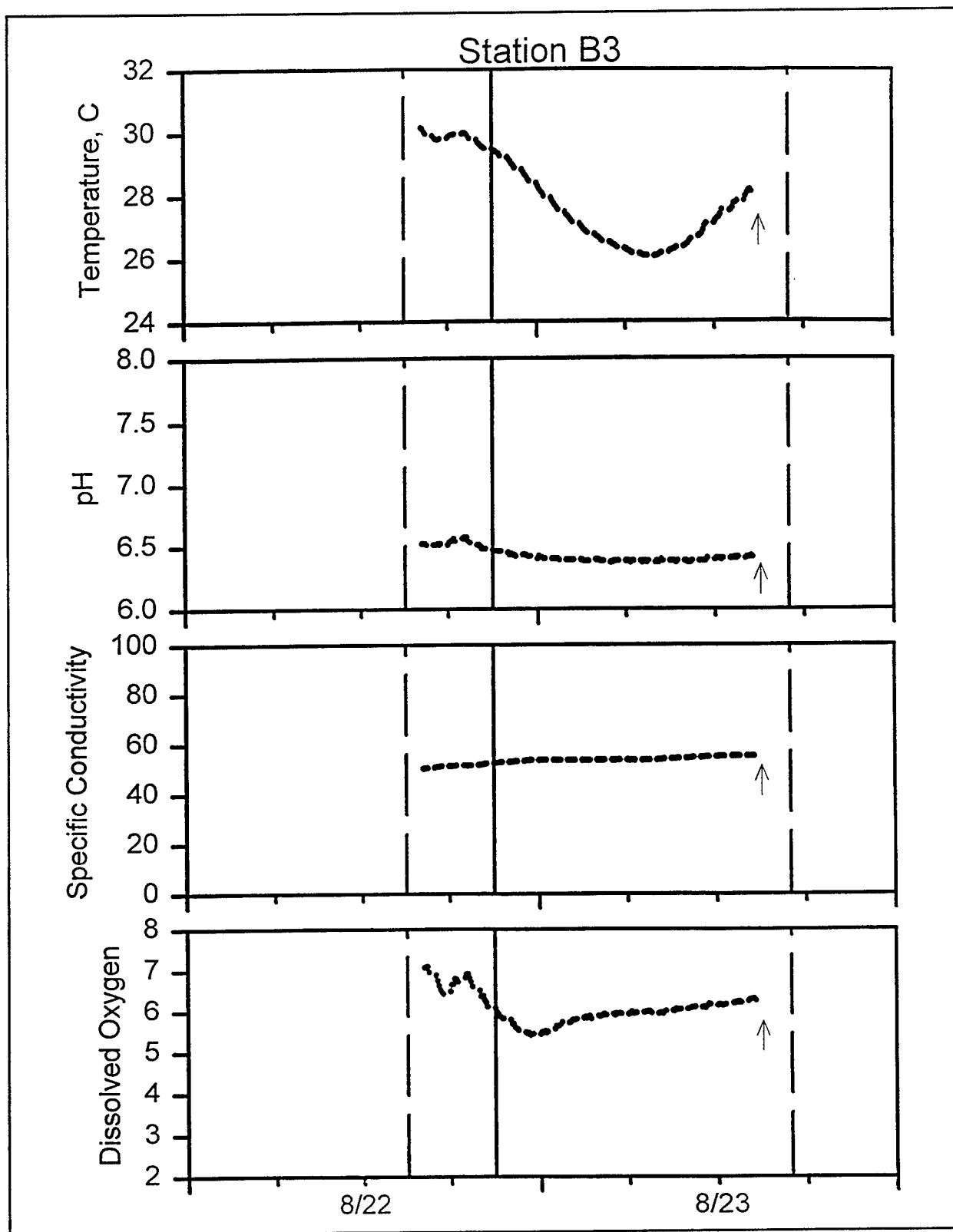


Figure 12. Temperature, pH, specific conductivity, and dissolved oxygen at Station B3 (Dashed line denotes steady-state discharge. Solid line denotes estimated travel time. Arrow denotes sampling time)

oxygen with another instrument upon completion of the study indicated that the continuous monitor underestimated dissolved oxygen concentrations. Considerable fouling of the membrane with an orange precipitate occurred at this site and may have contributed to the observed decrease in concentrations. Dissolved oxygen measurements conducted periodically at the site indicated that dissolved oxygen values were near $7 \text{ mg } \ell^{-1}$ throughout the high-flow release. At Station B1, diurnal effects were observed for temperature and pH, with maximum values occurring mid-afternoon except for lower pH observed on the afternoon of August 22, which reflected conditions prior to the arrival of the high-flow release. Temperature at Station B3 also reflected diurnal effects, but pH, specific conductivity, and dissolved oxygen remained relatively constant after arrival of the high-flow release.

Iron and manganese dynamics in the release from Nimrod Dam and Lake were evaluated with two methods. These methods used evaluation of oxidation states with colorimetric methods during the high-flow release at Stations A, B1, and B3 on filtered and unfiltered samples and evaluation of total and total soluble fractions at both the low-flow and high-flow releases. Each of these approaches provides different information. Evaluation of concentration changes of oxidation states, in conjunction with time of travel sampling, describes kinetics of the release water as it travels downstream. Differentiation of total and total soluble fractions, in conjunction with time of travel, allows description of particulate formation and comparison with concentration changes observed for oxidation states. Sampling during the low flow also provides information on particulate formation with increased residence time in the channel. Initial conditions were described with the single sample collected from the reservoir hypolimnion.

Iron in the reservoir bottom water was in the reduced ferrous (Fe^{2+}) form prior to release from the reservoir at a concentration near $17 \text{ mg } \ell^{-1}$ (Figure 13a). There was a decrease in both the total and ferrous Fe concentrations in the filtered samples, indicating the presence of some particulate Fe, primarily in the Fe^{2+} form. There was relatively good agreement in measurements on samples filtered through different pore sizes. Concentrations at Station A were considerably lower (near $1.8 \text{ mg } \ell^{-1}$) than those observed for the reservoir bottom water (Figure 13b), and ferric (Fe^{3+}) concentrations accounted for nearly 40 percent of the total in the unfiltered sample, indicating rapid oxidation of the ferrous iron. Differences in concentrations between the reservoir bottom water sample and the sample from Station A may be attributed to dilution of withdrawal water during release and possible loss of iron in the reach from the dam to Station A. Concentrations in the 0.1- and 0.2- μm filtered samples were similar but lower than concentrations in the 0.4- μm filtered samples, suggesting some size fractionation. However, most of the iron in all filtered samples was in the ferrous form. Differences in total iron (and ferrous iron) in the unfiltered and filtered samples suggest that particulate ferrous iron was present and represented 50 percent or more of the total ferrous iron. Greater concentrations of ferrous iron in the unfiltered sample suggest that filtration as a means to differentiate oxidation states may underestimate ferrous concentrations. At Station B1, total concentrations decreased to near $1 \text{ mg } \ell^{-1}$, which was nearly half that of concentrations at Station A, (Figure 13c), indicating removal of iron from the release water between these stations that is characterized as a pool. Concentrations in the unfiltered sample were nearly equally represented by ferrous

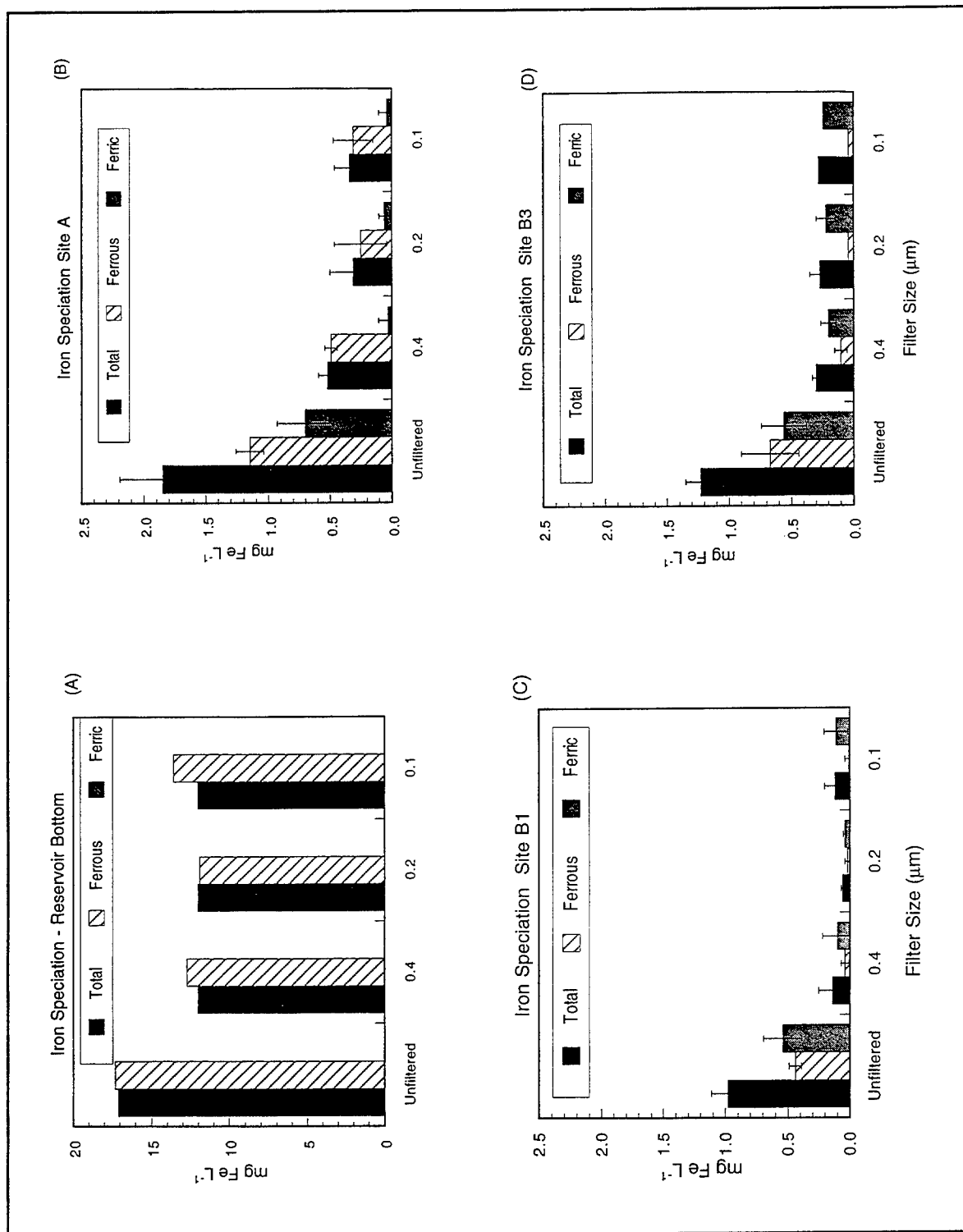


Figure 13. Iron speciation of reservoir release water at Lake Nimrod, Arkansas, August 1995

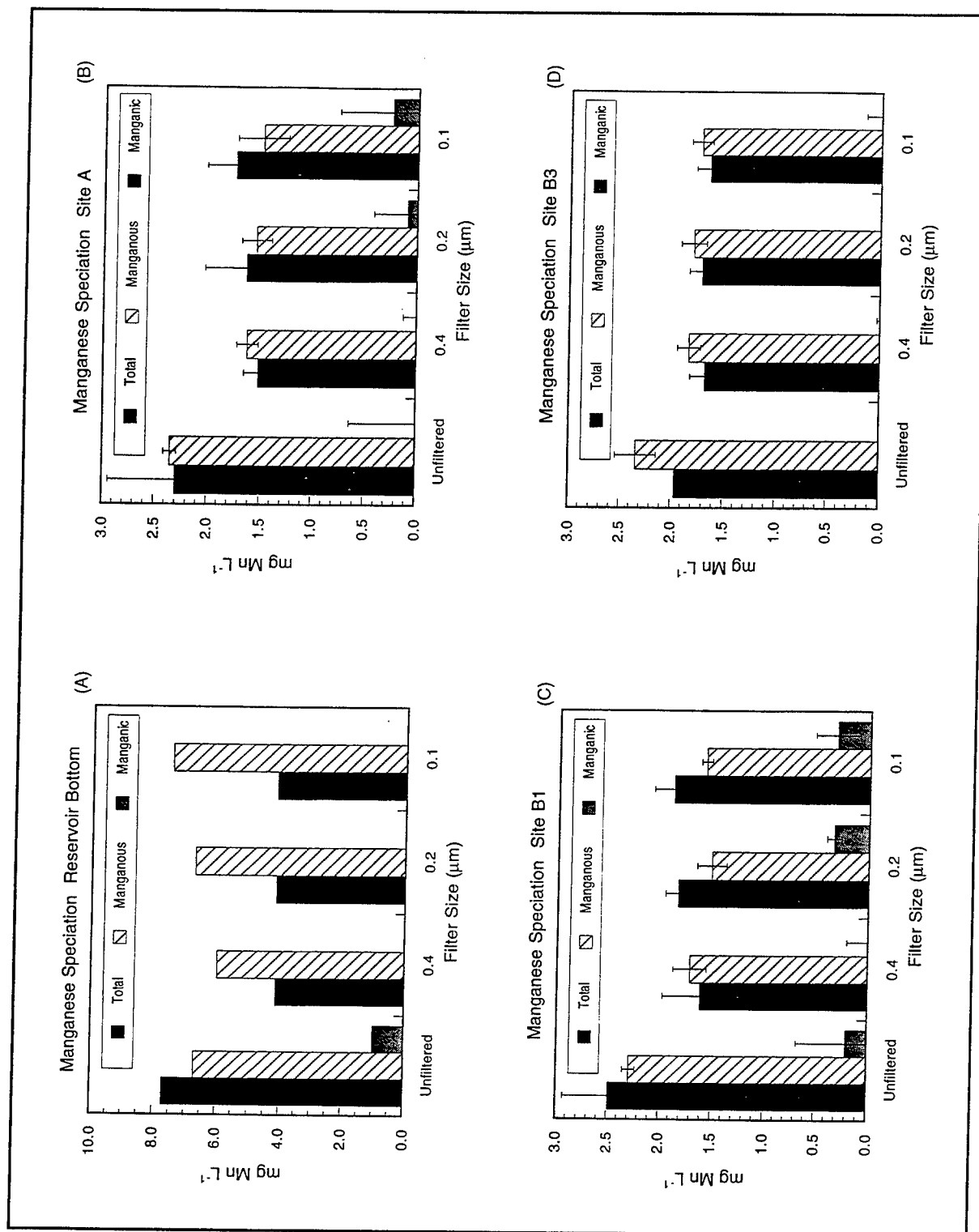


Figure 14. Manganese speciation of reservoir release water at Lake Nimrod, Arkansas, August 1995

and ferric forms and were considerably greater than concentrations in filtered samples, suggesting particulate fractions were predominant. A similar pattern was observed at Station B3 as that of Station B1 except that concentrations were slightly greater at Station B3 and ferric iron in the filtered samples was greater than ferrous concentrations (Figure 13d). Differences in concentrations between Stations B1 and B3 may be related to time of travel or resuspension associated with change in flow. Perhaps the best information is obtained in evaluation of the percent ferrous iron relative to the total in the unfiltered sample at each station. At Station A, ferrous iron represents about 62 percent of the total, and approximately 50 percent of the total at Stations B1 and B3, suggesting limited oxidation occurs between these two stations.

Manganese was in the reduced, manganous (Mn^{2+}) form in the reservoir bottom waters at a concentration near $8 \text{ mg } \ell^{-1}$ (Figure 14a). As was observed for iron, the observed concentration in the reservoir bottom waters was greater than downstream concentrations (Figure 14b through 14d) and may be attributed to dilution of bottom waters in the withdrawal zone during release and loss of manganese between the outlet and Station A. Higher concentrations of manganous Mn than total Mn in the sample from the reservoir bottom waters was attributed to pipetting errors since the artifact was not observed at the downstream stations. Concentrations at the downstream stations (A-B3) were between 1.5 and $2.5 \text{ mg } \ell^{-1}$ and decreased only slightly with distance in the unfiltered sample and remained relatively constant on all filtered samples. Differences in total and manganous Mn in the filtered and unfiltered samples in the release waters indicate the presence of some particulate manganous Mn.

Measurements of iron and manganese on unfiltered and filtered samples using ICP analyses provide additional information on iron and manganese dynamics at the two different release levels. Iron concentrations in the bottom waters of the reservoir were 17.3 and $15.3 \text{ mg } \ell^{-1}$ for total and total soluble iron (Figure 15), which compares with observations described above that indicated that the iron was primarily in the reduced, ferrous form. Concentrations were greater in the reservoir sample than at Station A for both release levels (as previously discussed), but total iron concentrations were much higher at all stations (i.e., $2\text{--}6 \text{ mg } \ell^{-1}$ compared with less than 2 when measured with ferrozine). Concentrations of total soluble iron, while in closer agreement with unfiltered samples analyzed with ferrozine, were still greater, suggesting an iron fraction detectable with ICP analyses that is not detected with ferrozine. Effects of flow were also apparent with concentrations of total iron, decreasing with distance from the dam during low flow while total soluble concentrations fluctuated between 1 and $2 \text{ mg } \ell^{-1}$. Concentrations of both total and total soluble remained relatively constant during the high-flow release with the exception of a slight increase in total soluble iron at Station B3. The decrease of total during low flow may be the result of oxidation and subsequent precipitation (this is supported by visual observations of an orange flocculent turbidity during low flow). At higher flows, precipitation is inhibited by increased velocities. Mechanisms contributing to fluctuations in total soluble are less readily apparent and may include sampling artifacts or size fractionation during oxidation and particulate formation.

Manganese concentrations in the bottom waters of the reservoir were near $3.4 \text{ mg } \ell^{-1}$ for both total and total soluble Mn (Figure 16), but were considerably

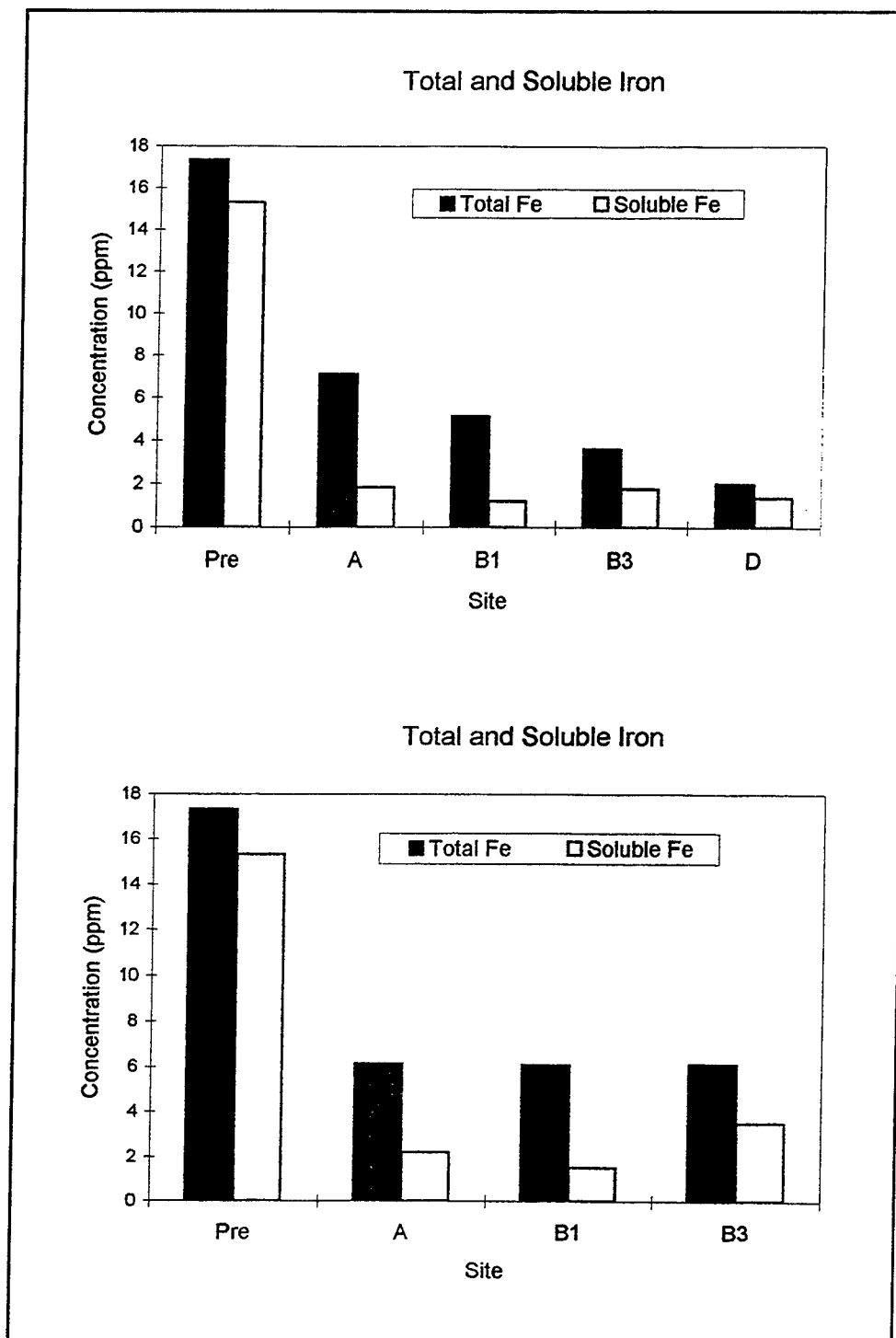


Figure 15. Total and soluble iron at lower (a) and higher (b) releases

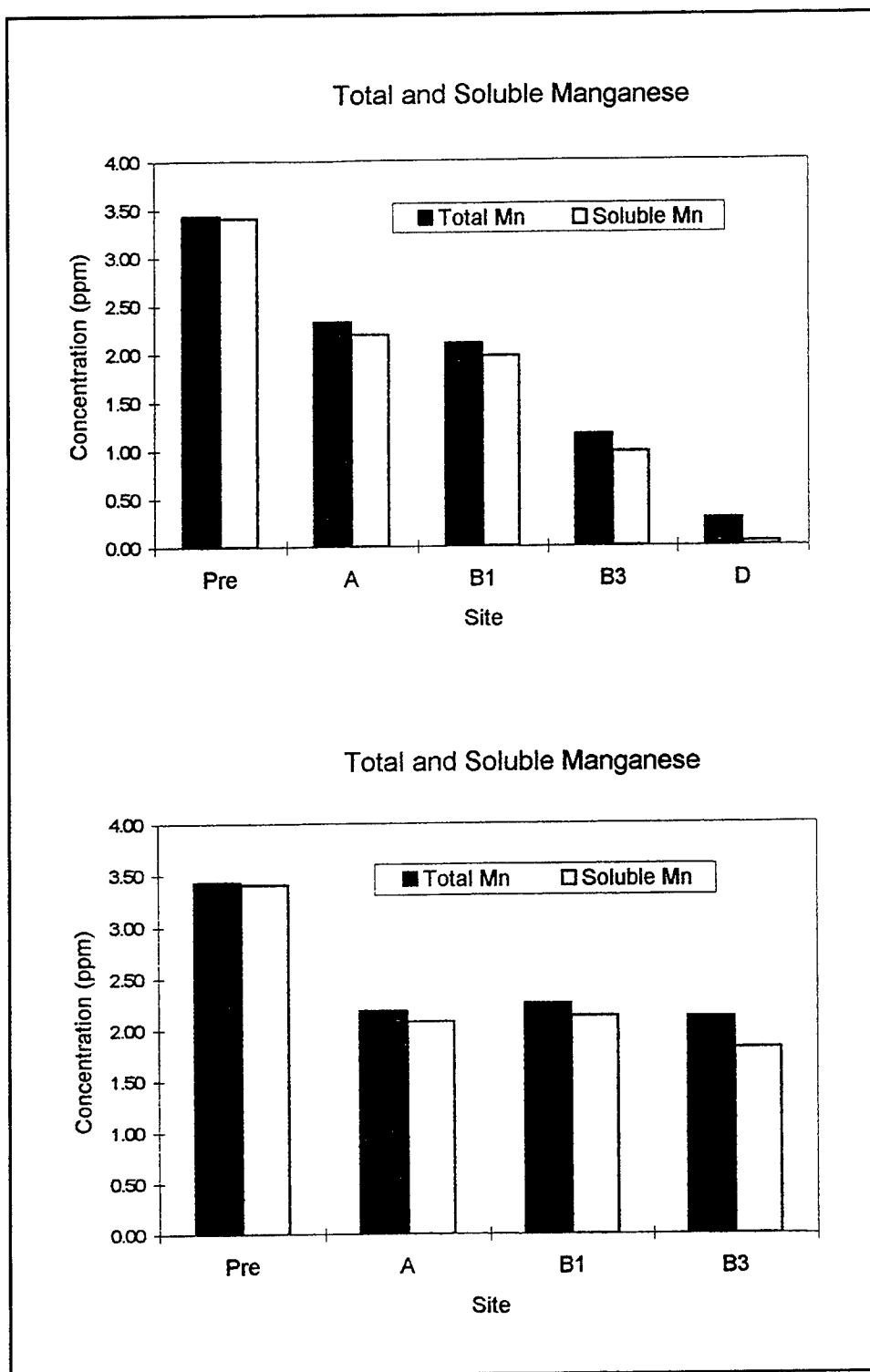


Figure 16. Total and soluble manganese at lower (a) and higher (b) releases

lower than observations made onsite with formaldoxime (see Figure 14). Concentrations in the release waters were in better agreement for the two different analytical methods when values of unfiltered samples analyzed with formaldoxime are used in the comparison. At the low-flow release, manganese concentrations decreased with distance from the dam, yet remained in the soluble form until well downstream (Station D), where insoluble manganese was predominant. During the higher flow release, concentrations remained relatively constant near $2.1 \text{ mg } \ell^{-1}$ and in the soluble form.

Results of the evaluation of photochemical ferric iron reduction indicated that photochemical reduction was not occurring at ambient release water pH values (6.8 to 7.2) (Figure 17). After 1800 hr, the samples were acidified to pH 3.0 with concentrated HNO_3 , and an increase in ferrous iron was then observed. The increase was much greater for the samples exposed to sunlight than those kept in the dark and is consistent with observations of photochemical reduction of iron in oxic water at lower pH values (near 4) and in the presence of organic matter (Collienne 1983). These results indicate that although photochemical reduction is possible, it is not a significant process in the Nimrod Dam release waters.

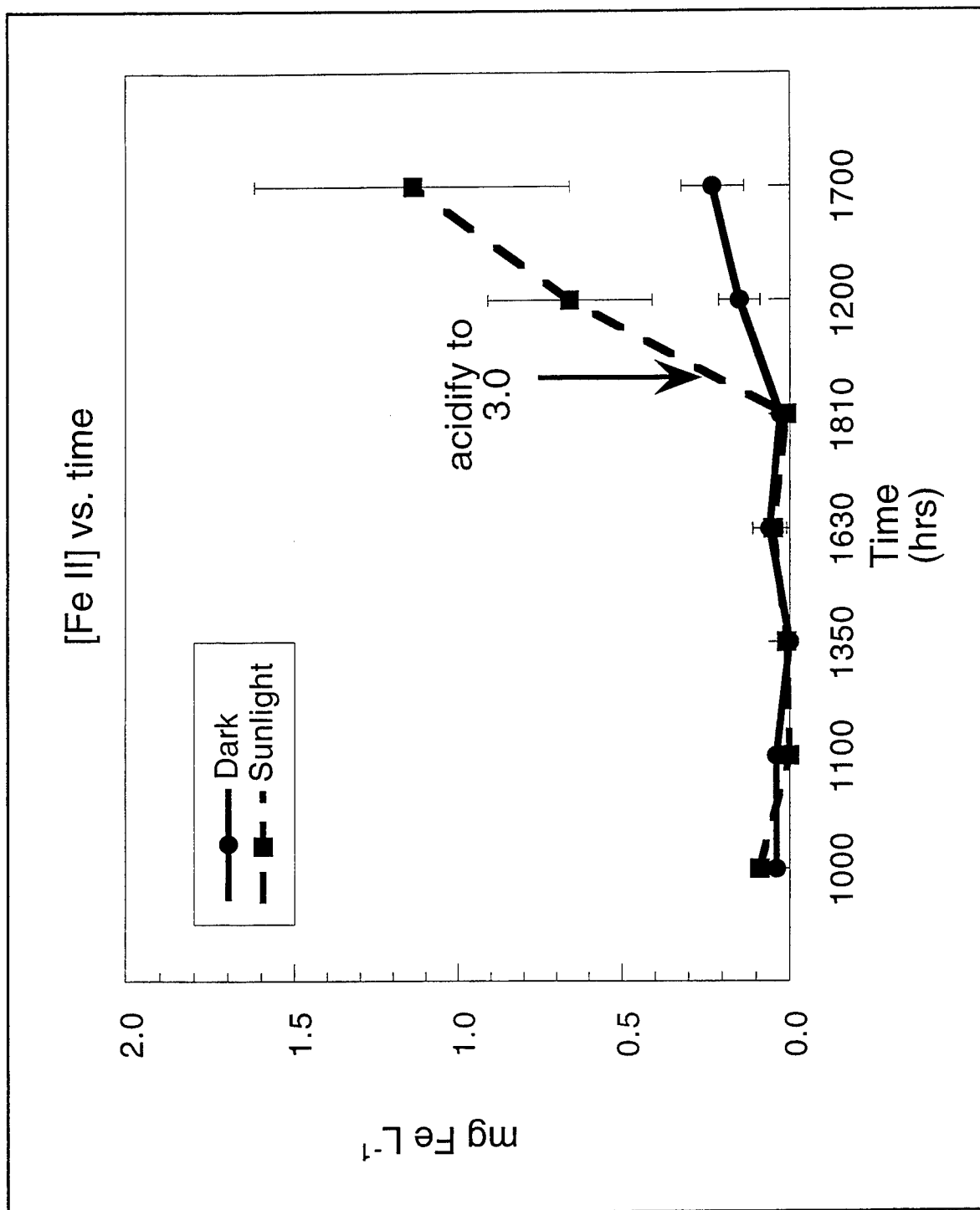


Figure 17. Results of photochemical reduction test of reservoir release water at Lake Nimrod, Arkansas

5 Conclusions and Recommendations

Speciation of iron and manganese for determining concentrations at different oxidation states for description of kinetics in reservoir releases was conducted with filtration and colorimetric methods. The use of colorimetric methods for measurement of iron concentrations in different oxidation states was determined to be applicable to field investigations. The use of ferrozine as a colorimetric reagent for measurement of ferrous (Fe^{2+}) iron with a portable colorimeter or spectrometer was considered to be an acceptable method. The use of filtration for speciation of iron (e.g., physical separation of oxidation states) was not supported by both laboratory and field studies. There were discrepancies in analytical methods used for the determination of total iron that affect the calculated concentration of ferric (Fe^{3+}). Determination of different oxidation states of manganese was considered possible for field studies using a colorimetric reagent (formaloxime) and filtration. For both iron and manganese, there were no differences among filter pore sizes.

The most applicable method for measurement of iron concentrations at different oxidation states uses the determination of total iron via laboratory analysis on an atomic adsorption spectrophotometer following digestion and the field determination of ferrous iron using ferrozine as a colorimetric reagent on an unfiltered sample. Ferric iron can then be determined via subtraction. Samples collected for total iron analysis should be preserved with sulfuric or nitric acid to a pH near 2 when collected.

The most applicable method for measurement of manganese concentrations at different oxidation states uses the determination of total manganese via laboratory analysis on an atomic adsorption spectrophotometer following digestion and the field determination of manganous manganese using formaloxime as a colorimetric reagent on an unfiltered sample. Oxidized manganese can then be determined via subtraction. The use of filtration to speciate oxidized from reduced via comparison with a total determination may also be applicable and is independent of filter pore size.

Analytical and field sampling techniques play a critical role in water quality studies of reservoir releases to the extent that if inappropriately conducted, data interpretation may be limited. A clear, well-defined objective for the study will help

determine the level of sampling and analytical methods required for an appropriate study. These recommendations are based on the assumption that field investigations are conducted by personnel with training in the field analytical techniques described, laboratory measurements such as atomic adsorption spectrophotometry are available, and an understanding of analytical interferences and water quality processes is applied during interpretation of the data from the study.

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Appendix A

Annotated References and General References

Annotated References

Boughriet, A., Ouddane, B., Fischer, J. C., Wartel, M., and Leman, G. (1992). "Variability of dissolved Mn and Zn in the Seine Estuary and chemical speciation of these metals in suspended matter," *Water Research* 26(10), 1359-78.

General study of dissolved and particulate forms of Mn and Zn. Analytical methods included graphite-furnace atomic adsorption spectroscopy, inductively coupled plasma-atomic emission spectroscopy, differential pulse anodic stripping voltammetry, and electron spin resonance spectroscopy for Mn. Considered salinity, pH, temperature, and total suspended matter and evolution of the metals with numerous soluble organic and inorganic ligands.

Boughriet, A., Ouddane, B., and Wartel, M. (1992). "Electron spin resonance investigations of Mn compounds and free radicals in particles from the Seine River and its estuary," *Marine Chemistry* 37, 149-69.

Describes a study using electron spin resonance spectroscopy that provided information on Mn(II), Mn(III), and Mn(IV) in particulates.

Brendel, P. J., and Luther, G. W., III. (1995). "Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, O₂, and S(-II) in porewaters of marine and freshwater sediments," *Environ. Sci. Tech.* 29, 751-61.

Describes the development of an electrode that can provide information on major redox species at submillimeter depths in porewaters of sediments using the fast scan of voltammetric methods for simultaneous measurement of major redox species during one potential scan.

Chin, C. S., Johnson, K. S., and Coale, K. H. (1992). "Spectrophotometric determination of dissolved manganese in natural waters with 1-(2-pyridylazo)-2-naphthol: Application to analysis in situ in hydrothermal plumes," *Marine Chemistry* 37, 65-82.

Describes spectrophotometric determination of dissolved manganese with 1-(2-pyridylazo)-2-naphthol. A detection limit of 22 nM was obtained in situ with a submersible chemical analyzer with rapid color development using flow injection.

Elrod, V. A., Johnson, K. S., and Coale, K. H. (1991). "Determination of subnanomolar levels of iron(II) and total dissolved iron in seawater by flow injection analysis with chemiluminescence detection," *Anal. Chem.* 63, 893-98.

Describes chemiluminescence detection of light emitted by the reaction of brilliant sulfoflavin with hydrogen peroxide and Fe(II) in a neutral medium using flow injection analysis that is highly sensitive (0.45 nmol L^{-1}) with a small sample volume (4.4 mL).

Grundl, T. (1992). "Redox inactivity of colloidal ferric oxyhydroxide solids," *Journal of Contaminant Hydrology* 9, 369-77.

Determined that colloidal (>6,000-8,000 daltons) ferric solids are redox inactive (may be dependent upon experimental conditions).

Grundl, T. J., and Macalady, D. L. (1989). "Electrode measurement of redox potential in anaerobic ferric/ferrous chloride systems," *Journal of Contaminant Hydrology* 5, 97-117.

Investigated the behavior of two inert redox electrodes (Pt and wax-impregnated graphite) and established a Nernstian response to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple for simple iron solutions at pH levels of 4 or less. Described a new method for determining dissolved ferric iron that permitted the calculation of Eh values that are independent of variations in the solubility of ferric oxyhydroxides.

Hart, B. T., Noller, B. N., Legras, C., and Currey, N. (1992). "Manganese speciation in Magela Creek, Northern Australia," *Aust. J. Mar. Freshwater Res.* 43, 421-41.

Described the removal of colloidal Mn as an aggregation with Ca and Mg as a function of the amount and characteristics of colloidal and particulate matter, Ca and Mg concentrations and turbulence in the creek.

Heron, G., Crouzet, C., Bourg, A. C. M., and Christensen, T. H. (1994). "Speciation of Fe(II) and Fe(III) in contaminated aquifer sediments using chemical extraction techniques," *Environ. Sci. Tech.* 28, 1698-705.

Describes single-step extractions including 1 M CaCl_2 , NaAc, oxalate, dithionite, Ti(III)-EDTA, 0.5 M HCl, 5 M HCl, hot 6 M HCl, and a sequential extraction by HI and Cr(II)HCl on standard iron minerals and nine aquifer sediments to determine oxidation states of Fe.

Hsiung, T. -M., and Tissue, T. (1994). "Manganese dynamics in Lake Richard B. Russell." *Environmental chemistry of lakes and reservoirs*. L. A. Baker, ed., American Chemical Society, Washington, DC, 499-524.

Describes Mn dynamics using electron spin resonance as analytical technique for measuring Mn(II) in reservoir waters.

King, D. W., Lounsbury, H. A., and Millero, F. J. (1995). "Rates and mechanisms of Fe(II) oxidation at nanomolar total iron concentrations," *Environ. Sci. Tech.* 29, 818-24.

Describes a fully automated luminol-based chemiluminescence system for rapid analysis of Fe(II) at natural levels. Measured rates of Fe(II) oxidation in 0.7 M NaCl for nanomolar concentrations at pH levels from 7.0 to 8.3.

Luther, G. W., III, and Ferdelman, T. G. (1993). "Voltammetric characterization of iron (II) sulfide complexes in laboratory solutions and in marine waters and porewaters," *Environ. Sci. Technol.* 27(6), 1154-63.

Describes investigations of metal sulfide complexes in marine waters and porewaters using voltammetric methods and comparisons with standard solutions with Fe(II) and sulfide.

Mallini, L. J., and Shiller, A. M. (1993). "Determination of dissolved manganese in seawater by flow injection analysis with colorimetric detection," *Limnol. Oceanogr.* 38(6), 1290-95.

Describes a flow-injection technique that was the Mn-catalyzed oxidation of iron by peroxide for colorimetric determination.

Spratt, H. G., Siekmann, E. C., and Hodson, R. E. (1994). "Microbial manganese oxidation in saltmarsh surface sediments using a leuco crystal violet manganese oxide detection technique," *Estuarine, Coastal and Shelf Science* 38, 91-112.

Describes use of the oxidation of 4,4',4"-methylidynetris (N,N-dimethylaniline), leuco crystal violet (LCV) by Mn oxides to produce crystal violet. The authors report that the assay exhibits high specificity for Mn oxides without interference by Mn(II) and is sufficiently sensitive to determine rates of Mn oxidation in surface sediment or saltmarsh creek water suspensions.

Yi, Z., Zhuang, G., Brown, P. R., and Duce, R. A. (1992). "High-performance liquid chromatographic method for the determination of ultratrace amounts of iron(II) in aerosols, rainwater, and seawater," *Anal. Chem.* 64, 2826-30.

Describes a reversed-phase high performance liquid chromatography method developed to determine Fe(II) in low concentrations using ferrozine.

Young, L. B., and Harvey, H. (1992). "The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments," *Geochim. Cosmochim. Acta* 56, 1175-86.

Describes the sorption of Zn, Ni, and Cu by surficial sediments in four acid (pH < 5.6) and three circumneutral (pH 6.4-6.5) lakes using recovery from easily reducible (exchangeable and bound to oxides of Mn), reducible (bound to oxides of Fe), and alkaline extracted (organically bound) fractions of sediment. Some description of a concurrent pH-induced precipitation of Fe-humic complexes involving the coprecipitation of trace metals with strongly bound Fe-humic complexes.

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13. ABSTRACT (Maximum 200 words) Techniques for assessing the fate of selected chemical constituents in reservoir tailwaters were evaluated using a review of analytical methods and laboratory studies to determine applicable field methods and field studies to evaluate selected methods. An annotated bibliography of analytical methods is included. Analytical methods for the measurements of reduced and oxidized iron and manganese were the primary methods evaluated. Colorimetric methods using ferrozine were determined the most suitable for measurements of reduced iron. Colorimetric measurements of manganese using formaldoxime were considered the most suitable for measurements of reduced manganese. Filtration, a commonly used method to differentiate reduced and oxidized forms of iron and manganese in field applications, was considered inadequate, especially for reduced iron determinations. Field sampling recommendations included the use of colorimetric methods for real-time measurements of reduced iron and manganese and sample collection and preservation for laboratory analyses for measurements of total iron and manganese. Concentrations of oxidized iron and manganese can then be calculated by difference. A case study conducted at Nimrod Lake, a flood control reservoir in central Arkansas, using recommended colorimetric techniques supported laboratory investigations. Recommended analytical methods for measuring reduced iron and manganese will improve application and interpretation of the Tailwater Quality Model for describing water quality processes in reservoir releases.				
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